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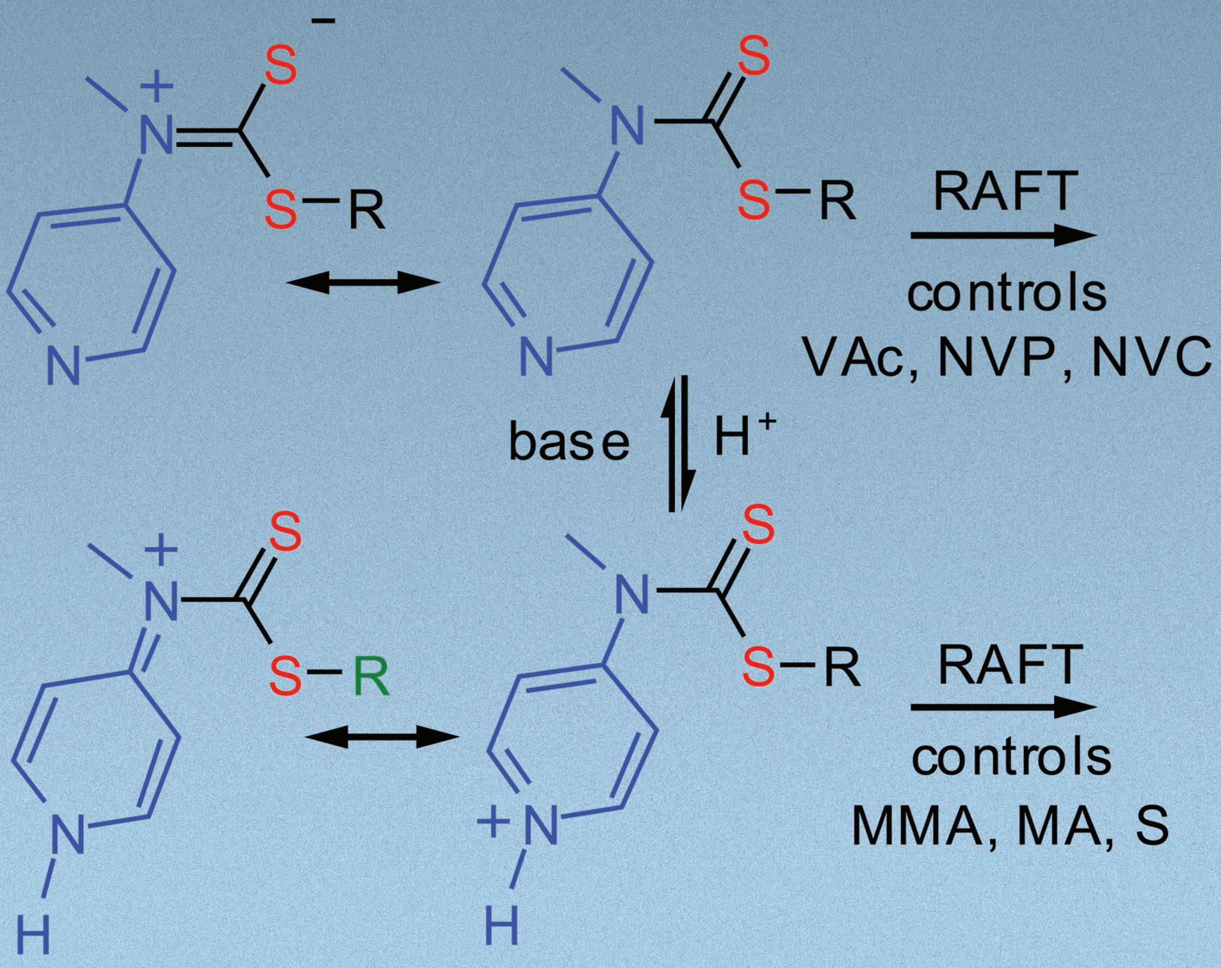
Materials of the Future, Science of Today: Radical Polymerization – The Next Stage



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Foreword

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Aust. J. Chem. **2010**, *63*, 1

RAFT Polymerization – The Compilation

Graeme Moad, Ezio Rizzardo, and San H. Thang

Radical polymerization is one of the most widely used processes for the commercial production of high molecular weight polymers. The past 15 years has seen the emergence of effective techniques for implementing radical polymerization characteristics associated with living polymerization. Thus we (Fig. 1) have a set of tools that allow unprecedented control over the process and the polymer product while retaining much of the versatility of conventional radical polymerization. Radical polymerization with reversible addition–fragmentation chain transfer (RAFT) is foremost among these tools.

The first review,[1] originally published in 2005, describes the historical development of RAFT and provides and introductory guide to the use of the technique illustrated by examples from our own work. The second[2] and third reviews[3] provide a comprehensive survey of developments in the method covering the periods 2005–2006 and 2006–2009 respectively.

The publication rate on RAFT polymerization continues to increase. While there remains substantial scope for increasing our understanding of the process, the change in focus from the study of the scope and mechanism of RAFT polymerization towards applications of the process is clearly evident. RAFT polymerization, in providing a tool to manipulate molecular architecture of polymers, means that it is no longer a formidable task to apply radical polymerization to the synthesis of blocks, stars, or other polymers of complex architecture. RAFT polymerization is being employed to facilitate the current revolution in those areas of materials science grouped under the nanotechnology umbrella and we can anticipate that new materials with the potential to further revolutionize polymer industry will continue to appear. Our first RAFT patent[4] appeared seventh in the list of most cited patent families for 2005 in chemistry and related science published by Chemical Abstracts Service's Science Spotlight.[5] This is emphasized by the fact that there are now over 100 companies that have taken out patents that relate to the RAFT process or its applications. This activity currently accounts for over 370 distinct patent applications and over 150 granted US patents.

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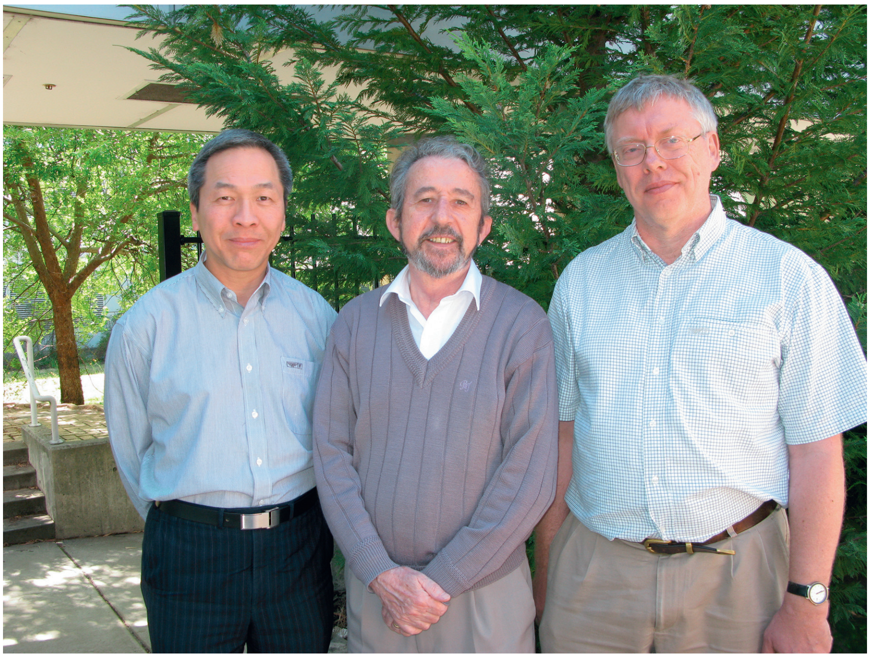

Fig. 1. San H. Thang, Ezio Rizzardo, and Graeme Moad (left to right).

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The RAFT Alliance, a Global Community Promoting Innovation

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Reversible addition–fragmentation chain transfer (RAFT) chemistry was first published in 1998 by CSIRO scientists Ezio Rizzardo, Graeme Moad, and San Thang.[1] RAFT is a powerful polymerization technology for the synthesis of tailor-made polymers with predetermined molecular weights, with narrow polydispersities, and with highly complex architectures.[2]

Continued research into fundamental RAFT chemistry has seen the development of intellectual property in the order of some 300 patents,[3] all based upon the original[4] patent from CSIRO, Australia's national research organization. Key developments of the RAFT technology, such as end-group removal,[5–8] microgel synthesis,[9] and aqueous polymerization,[10,11] have been integral to the development of innovative applications. These include coatings with improved pigment dispersions,[12] lubricants to improve fuel economy,[13] and spatially controlled drug conjugates.[14] There is an ever-increasing demand for technical and commercial information to support the applications of RAFT in industry. At CSIRO, we have initiated the RAFT Alliance; a community of scientists and business professionals with shared research or commercial interests in RAFT (Fig. 1). The RAFT Alliance was launched at the inaugural RAFT Symposium in 2009.[15] This fostered social and technical collaboration in the global RAFT community.

Presentations and publications describing the development in RAFT can be accessed on the RAFT Alliance website (http://teams.csiro.au/sites/RAFT/default.aspx). The RAFT Alliance site allows questions to be posed to members, and solutions to be presented. The RAFT Alliance already has over 100 members.

Companies that network with other organizations, including research institutions and their customers, have been shown to have greater success in both process and product innovation.[16] The success of such networks has been attributed to the addition of new information and knowledge, and the opportunity for collaboration.[17]

Access to networks, such as the RAFT Alliance, fosters greater knowledge transfer and accelerated learning. Social functions will be organized at key polymer conferences such as the Pacific Polymer Conference (Cairns, Australia, 2009), the American Chemical Society 239th National Meeting (San Francisco, USA, 2010), and the 43rd IUPAC World Polymer Congress (Macro2010, Glasgow, UK).

Fig. 1. Heather Maynard (UCLA), Ezio Rizzardo (CSIRO), Charles McCormick (University of Southern Mississippi), Sebastian Perrier (University of Sydney), and Tom Davis (University of New South Wales) at the February 2009 RAFT Symposium, held in honour of Ezio Rizzardo's 65th Birthday, where the RAFT Alliance was first launched.

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Fig. 2. Ulrich Schubert (University of Jena), Stephanie Hornig (University of California, Berkeley), Kate Dawson (CSIRO), and Tim O'Meara (CSIRO) at the recent RAFT Alliance 'Meet and Greet' held during the American Chemical Society 238th National Meeting, Washington, 2009.

The RAFT Alliance 'Meet and Greet' held during the American Chemical Society 238th National Meeting (Washington, USA, August 2009) was highly successful (Fig. 2). Our next satellite event is to be held in December in Cairns, at the Pacific Polymer Conference. This upcoming 'Meet and Greet' is free for RAFT Alliance members. Contact Kate Dawson for more information on the RAFT Alliance, or sign up via http://www.csiro.au/services/RAFT-Alliance-Sign-Up.html.

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Review

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Aust. J. Chem. **2005**, *58*, 379–410

Living Radical Polymerization by the RAFT Process

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This paper presents a review of living radical polymerization achieved with thiocarbonylthio compounds [ZC(=S)SR] by a mechanism of reversible addition–fragmentation chain transfer (RAFT). Since we first introduced the technique in 1998, the number of papers and patents on the RAFT process has increased exponentially as the technique has proved to be one of the most versatile for the provision of polymers of well defined architecture. The factors influencing the effectiveness of RAFT agents and outcome of RAFT polymerization are detailed. With this insight, guidelines are presented on how to conduct RAFT and choose RAFT agents to achieve particular structures. A survey is provided of the current scope and applications of the RAFT process in the synthesis of well defined homo-, gradient, diblock, triblock, and star polymers, as well as more complex architectures including microgels and polymer brushes.

Manuscript received: 18 March 2005.
Final version: 3 May 2005.

Introduction

Radical polymerization is one of the most widely used processes for the commercial production of high-molecular-weight polymers.[1] The main factors responsible for the pre-eminent position of radical polymerization are that: (*a*) it can be used with a large variety of monomers including (meth)acrylates, styrene, (meth)acrylamides, butadiene, and vinyl acetate; (*b*) it is tolerant to a wide range of functional groups (e.g. OH, NR_2, COOH, $CONR_2$) and reaction conditions (bulk, solution, emulsion, miniemulsion, suspension); and (*c*) it is simple to implement and inexpensive in relation to competitive technologies. However, the conventional process has some notable limitations with respect to the degree of control that can be asserted over macromolecular structure, in particular, the molecular weight distribution, composition, and architecture.

The recent emergence of techniques for implementing living radical polymerization has provided a new set of tools for polymer chemists that allow very precise control over the polymerization process while retaining much of the versatility of conventional radical polymerization.[2–8] It is no longer a formidable task to apply radical polymerization to

Graeme Moad obtained his B.Sc.(Hons1) in 1974 and Ph.D. in 1977 from the University of Adelaide in the field of organic free radical chemistry. Between 1977 and 1979 he undertook postdoctoral research at Pennsylvania State University in the field of biological organic chemistry. He joined CSIRO as a research scientist in 1979 and is currently a chief research scientist. Dr Moad is coauthor of the book 'The Chemistry of Free Radical Polymerization' which is about to go to a second edition. His research interests lie in the fields of polymer design and synthesis (free radical polymerization, reactive extrusion), polymerization kinetics and mechanism, and most recently polymer nanocomposites.

Ezio Rizzardo is a graduate of the University of New South Wales and received his Ph.D. from the University of Sydney for his studies on the photochemistry of nitro compounds. He joined CSIRO in 1976 after a postdoc at Rice University, RIMAC, and the Australian National University. His CSIRO research has focussed on developing methods for controlling free radical polymerization. For this he has received a number of awards including the RACI Australian Polymer Medal and the CSIRO Chairman's Gold Medal. Currently he is a CSIRO Fellow and a Fellow of the Australian Academy of Science.

San H. Thang was born in Saigon, Vietnam, in 1954 and came to Australia in 1979 as a refugee. He completed his B.Sc.(Hons) degree in 1983 and Ph.D. in 1987 from Griffith University. He joined CSIRO in 1986 as a research fellow. He then moved to ICI Australia in late 1987 to undertake the challenge of industrial research. He returned to CSIRO in late 1990, and in 1995 he was co-inventor of the RAFT Process. He is currently a senior principal research scientist at CSIRO Molecular Science where his research focusses on the interface between organic and polymer chemistry.

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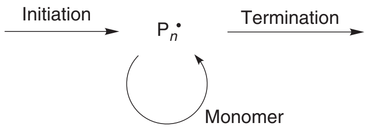
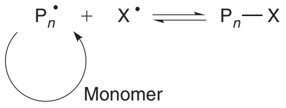
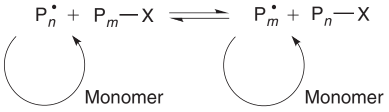


Scheme 1.



Scheme 2. Reversible deactivation.



Scheme 3. Reversible chain transfer.

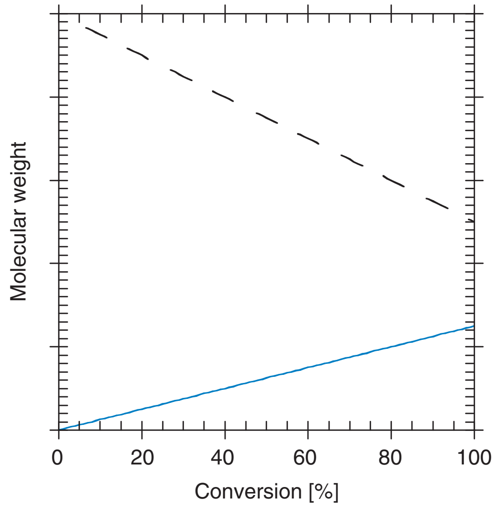


Fig. 1. Evolution of molecular weight with monomer conversion for a conventional radical polymerization with constant rate of initiation (– – –) and a living radical polymerization (—).

the synthesis of blocks, stars, or other polymers of complex architecture. New materials that have the potential of revolutionizing a large part of the polymer industry are beginning to appear. Possible applications range from novel surfactants, dispersants, coatings, and adhesives, to biomaterials, membranes, drug delivery media, and materials for microelectronics.

To understand how RAFT and other forms of living radical polymerization work, we first need to consider the mechanism of the conventional process.[1] Radical polymerization is a chain reaction. The chains are initiated by radicals (formed from an initiator) adding to monomer. Chain propagation then involves the sequential addition of monomer units to the radical ($P_n^\bullet$) so formed. Chain termination occurs when the propagating radicals react by combination or disproportionation. A much simplified mechanism is shown in Scheme 1.

In conventional radical polymerization, the steady-state concentration of propagating species is about 10^{-7} M, and individual chains grow for 5–10 s before terminating. Chains are continuously formed, propagate, and are terminated by radical–radical reaction. The molecular weight of chains formed in the early stages of polymerization is high and will reduce with conversion because of monomer depletion (Fig. 1). The breadth of the molecular-weight distribution and polydispersity is governed by statistical factors. The polydispersity, expressed in terms of the ratio of weight to number average molecular weights,* is broad ($\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n} > 1.5$; see Fig. 2).

In an ideal living polymerization, all chains are initiated at the beginning, grow at the same rate, and survive the polymerization (there is no termination). The propensity of free radicals to undergo radical–radical termination means that, for the case of radical polymerization, all chains cannot be simultaneously active. To confer living character on a radical polymerization, it is necessary to suppress or render insignificant all processes that terminate chains irreversibly. Thus, living radical polymerization only becomes possible in the presence of reagents that react with the propagating radicals ($P_n^\bullet$) by reversible deactivation (Scheme 2) or reversible chain transfer (Scheme 3) so that the majority of chains are maintained in a dormant form (P_n—X). The average concentration of the active propagating species in a living radical polymerization may be similar to that for the conventional process although the cumulative lifetime of an individual chain as an active species will be lower. Rapid equilibration between the active and dormant forms ensures that all chains possess an equal chance for growth and that all chains will grow, albeit intermittently. Under these conditions, the molecular weight increases linearly with conversion (Fig. 1) and the molecular weight distribution can be very narrow (e.g. $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n} \approx 1.1$, Fig. 2).

The living radical polymerization techniques that have recently received greatest attention are nitroxide-mediated polymerization (NMP), atom-transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT). The NMP technique was devised in our laboratories in the early 1980s,[10] and in recent years has been exploited extensively for the synthesis of narrow molecular-weight distribution homopolymers and block copolymers of styrene and acrylates.[2,11,12] Recent developments have made NMP applicable to a wider, though still restricted, range of monomers.[2] ATRP is substantially

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*The number average molecular weight or molar mass is simply the total weight of the sample divided by the number of molecules in the sample: $\overline{M}_\mathrm{n} = \sum n_i M_i / \sum n_i = \sum w_i / \sum n_i$, where n_i is the number of chains of length i, w_i is the weight of chains of length i, and M_i is the molecular weight of a chain of length i. The weight average molecular weight is the sum of the weights of chains of each molecular weight multiplied by their molecular weight divided by the total weight of the sample: $\overline{M}_\mathrm{w} = \sum w_i M_i / \sum w_i = \sum n_i M_i^2 / \sum n_i M_i$. The weight average is always greater than the number average molecular weight. The polydispersity is the ratio of the weight average to the number average molecular weight and, for an ideal radical polymerization, will be 2 for termination by disproportionation or chain transfer, or 1.5 for termination by combination.

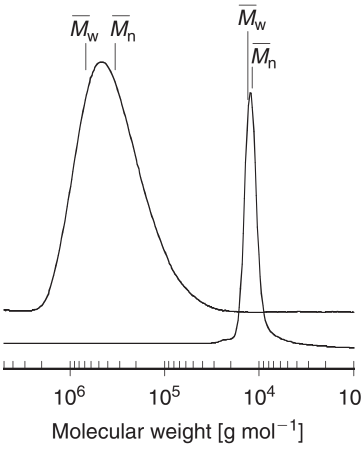


Fig. 2. Typical molecular weight distributions for a conventional and living radical polymerization. Data shown are from GPC analysis of polystyrene prepared by thermal polymerization of styrene at 110°C for 16 h ($\overline{M}_n$ 324000, $\overline{M}_w/\overline{M}_n$ 1.74, 72% conversion) and a similar polymerization in the presence of cumyl dithiobenzoate (0.0029 M) ($\overline{M}_n$ 14400, $\overline{M}_w/\overline{M}_n$ 1.04, 55% conversion).[9]

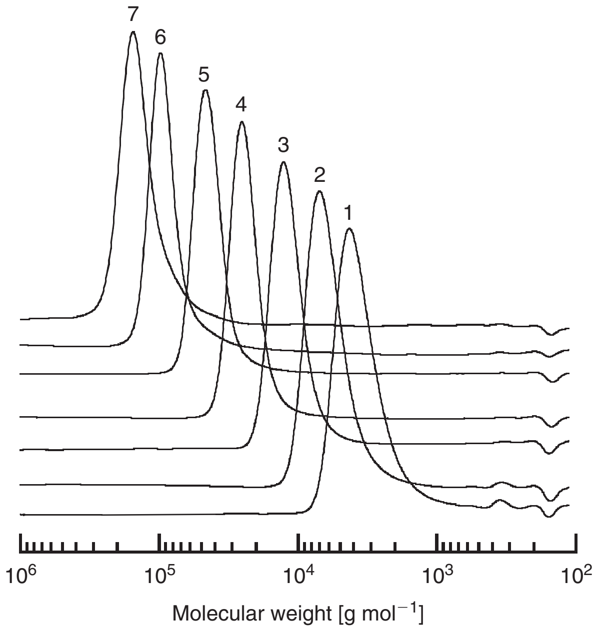


Fig. 3. GPC traces of PMMA formed by polymerization of MMA (6.55 M in benzene) with 1,1′-azobis(1-cyclohexanenitrile) (0.0018 M) as initiator and various concentrations of RAFT agent **64** for 6 h at 90°C (refer to Table 1 for details).[15]

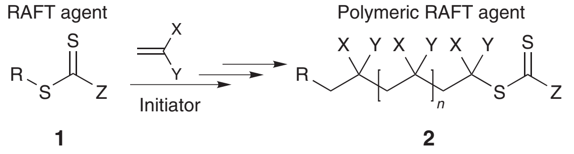
more versatile;[3,4] however, it requires unconventional initiating systems that often have poor compatibility with polymerization media. RAFT polymerization, also devised in our laboratories,[13,14] is one of the most recent entrants in this field and arguably the most convenient and versatile.[5–7]

In this paper, we report on the development, scope and mechanism of living radical polymerization with reversible addition–fragmentation chain transfer. The paper will emphasize research carried out at CSIRO but is augmented by the work of other groups, where appropriate, to provide a more complete picture.

Table 1. Molecular weights and polydispersities for PMMA formed by polymerization of MMA (6.55 M in benzene) with 1,1′-azobis(1-cyclohexanenitrile) (0.0018 M) as initiator and RAFT agent 64 for 6 h at 90°C[15]

Trace	$[\mathrm{RAFT}]_o$ [M × 10^2]	$\overline{M}_n$^{A} [g mol^{-1}]	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$(calc.)^B [g mol^{-1}]	Conversion [%]
1	19.92	2870	1.18	3000	80
2	9.96	5040	1.14	5600	80
3	4.95	9940	1.12	10400	79
4	2.48	21800	1.13	22600	91
5	1.24	41100	1.14	45300	>99
6	0.61	80900	1.13	80100	>99
7	0.32	126000	1.15	125000	>99

^{A} Values rounded off to three significant figures.
^{B} Based on Eqn 5 and an assumed cumulative initiator efficiency (f) of 0.3.



Scheme 4. Overall reaction in RAFT polymerization.

RAFT Polymerization

The utility of the RAFT process is illustrated by the following example of RAFT polymerization of methyl methacrylate (MMA). A series of MMA polymerizations were carried out at 90°C with 1,1′-azobis(1-cyclohexanenitrile) initiator, and using an approximate 60-fold range of concentrations of *S*-dodecyl *S*-(2-cyano-4-carboxy)but-2-yl trithiocarbonate **64** (see Table 5).[15] The molecular weight distributions observed after six hours are shown in Fig. 3. The molecular weights, ranging from 2870 to 126000, agree with expectation based on the concentrations of RAFT agent and initiator used (Table 1). All samples have narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n < 1.2$).

The main features of the ideal RAFT polymerization can be summarized as follows.

- RAFT polymerization (Scheme 4) can be performed by simply adding a chosen quantity of an appropriate RAFT agent to a conventional free-radical polymerization. The same monomers, initiators, solvents, and temperatures are used.
- RAFT polymerization possesses the characteristics usually associated with living polymerization. All chains begin growth at the commencement of polymerization and continue to grow until the monomer is consumed. Molecular weights increase linearly with conversion (Fig. 1). Active chain ends are retained.
- Molecular weights in RAFT polymerization can be predicted using Eqn 1

$$\overline{M}_n(\mathrm{calc}) \approx \frac{[\mathrm{M}]_o - [\mathrm{M}]_t}{[\mathbf{1}]_o} m_\mathrm{M} \qquad (1)$$

where $[\mathrm{M}]_o - [\mathrm{M}]_t$ is the monomer consumed and m_M is the monomer molecular weight.

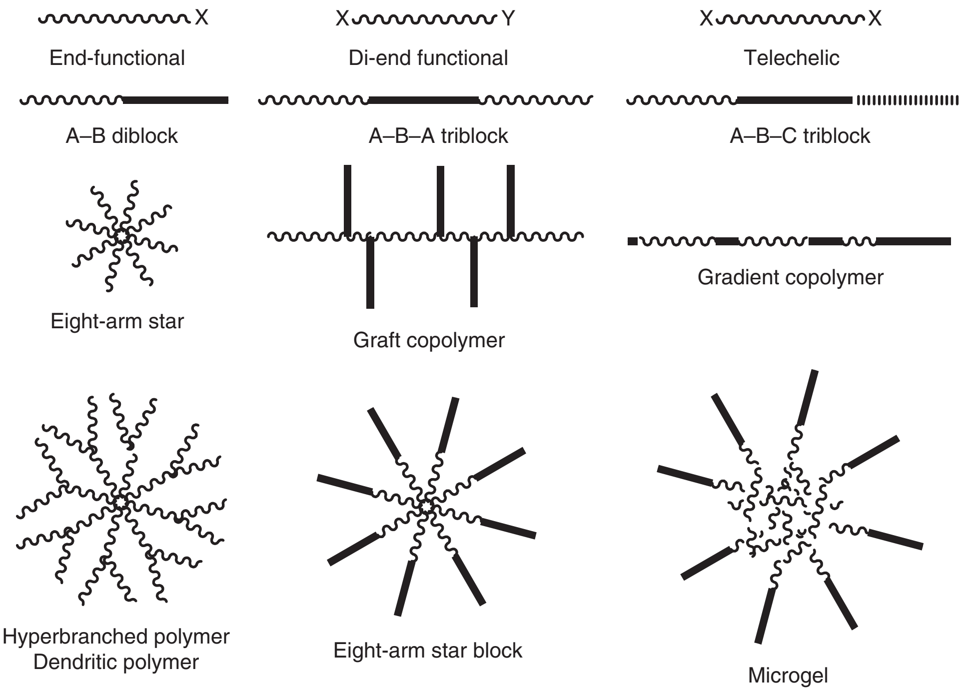


Fig. 4. Polymer architectures.

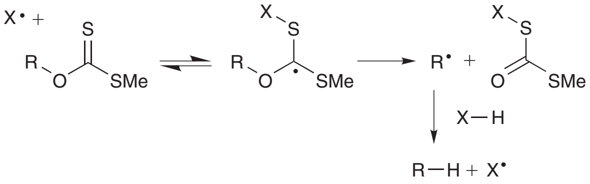
- Narrow molecular weight distributions are achievable (Fig. 2).
- Blocks, stars, and complex molecular architectures are accessible (Fig. 4).

With appropriate selection of the RAFT agent for the monomers used and the reaction conditions, all or most of the above can be routinely achieved. An understanding of the mechanism of RAFT polymerization provides insight and allows the formulation of some simple guidelines for successfully implementing RAFT polymerization.

History of RAFT

Although the acronym RAFT[13] can be used in a more general sense, it has come to be closely associated with radical polymerizations carried out in the presence of thiocarbonylthio compounds which react by reversible addition–fragmentation chain transfer.

The same process when it involves xanthate RAFT reagents is sometimes also called MADIX (macromolecular design by interchange of xanthate).[16] Reversible addition–fragmentation chemistry involving xanthate esters has been known to organic chemists for some time. It forms the basis of the Barton–McCombie process for deoxygenation of alcohols (Scheme 5).[17–19] Note that the process relies on selective cleavage of the R—O bond. The deoxygenation pathway is facilitated by formation of a strong C=O bond, but it is also important that the group on sulfur is chosen to be a poor homolytic leaving group (typically methyl or ethyl). X—H in Scheme 5 is usually tri-*n*-butyl stannane, but other free-radical reducing agents[20] may also be used. When the group on sulfur is a good homolytic leaving group (a propagating radical), chemistry similar to that involved in the Barton–McCombie reaction can be used to desulfurize thiols and to cleave RAFT end groups (see later).

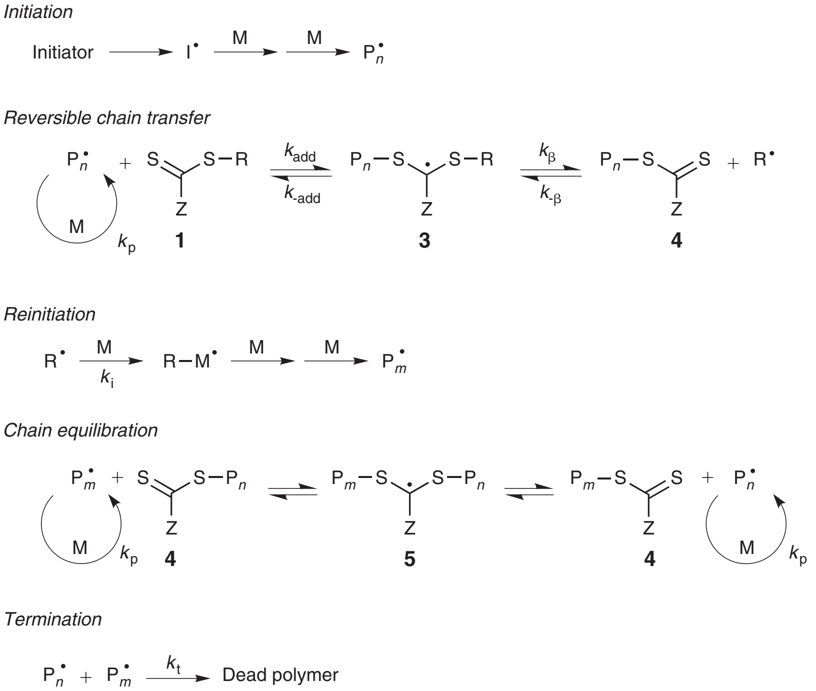


Scheme 5.

In 1988, Zard and coworkers[21] first proposed xanthate esters and reversible chain transfer as a convenient source of alkyl radicals and applied this chemistry in the synthesis of monoadducts to a monomer (a maleimide). Numerous applications of xanthate addition fragmentation chemistry in organic synthesis have been described in papers and reviews by the same group.[22,23]

We first reported the use of addition–fragmentation chain transfer agents to control polymerization in the mid 1980s.[7,32,33] The agents include macromonomers,[24–26] allyl sulfides,[27] allyl bromides,[28] allyl peroxides,[29] vinyl ethers,[30] and thionoesters.[31] We also reported that living characteristics (narrow polydispersities, block synthesis) could be achieved with the use of macromonomer RAFT agents in emulsion polymerization of methacrylate monomers in 1995 (the acronym RAFT was not used at that time).[34,35]

Living radical polymerization using thiocarbonylthio RAFT agents was first described in a patent published in 1998.[14] The first paper and conference reports describing the process also appeared in 1998.[13] Other patents[36–38]



Scheme 6. Mechanism of RAFT polymerization.

and papers soon followed. This method, along with NMP and ATRP, now dominates the literature on living radical polymerization and radical polymerization generally.[39,40] As of January 2005, the first paper on RAFT[13] had received more than 500 citations (Scifinder). The RAFT patent[14] was the ninth most cited in the field of Chemistry and Related Science in 2003 and the most cited of those published within the last ten years (Chemical Abstracts Service).[41]

Mechanism of RAFT

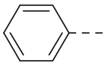
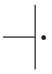
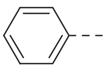
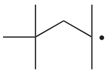
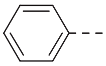
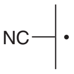
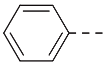
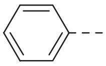
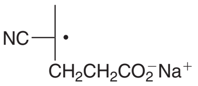
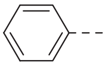
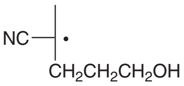
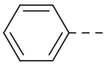
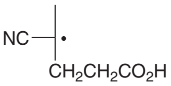
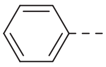
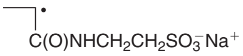
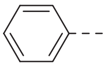
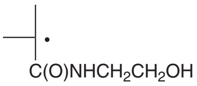
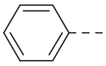
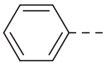
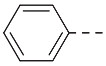
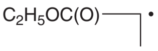
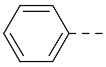
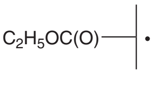
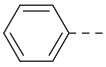
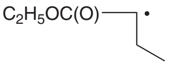
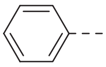
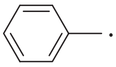
The key feature of the mechanism of RAFT polymerization is a sequence of addition–fragmentation equilibria as shown in Scheme 6.[5,13] Initiation and radical–radical termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical ($P_n^\bullet$) to the thiocarbonylthio compound [RSC(Z)=S, **1**] followed by fragmentation of the intermediate radical gives rise to a polymeric thiocarbonylthio compound [P_nS(Z)C=S, **4**] and a new radical (R$^\bullet$). Reaction of the radical (R$^\bullet$) with monomer forms a new propagating radical ($P_m^\bullet$). Rapid equilibrium between the active propagating radicals ($P_n^\bullet$ and $P_m^\bullet$) and the dormant polymeric thiocarbonylthio compounds **4** provides equal probability for all chains to grow, and allows for the production of polymers with narrow polydispersity. When the polymerization is complete (or stopped), most of chains retain the thiocarbonylthio end group and can be isolated as stable materials.

The mechanism for achieving control in RAFT polymerization differs significantly from that involved in NMP and ATRP. The latter processes involve reversible deactivation of propagating radicals by radical–radical reaction (NMP) or atom transfer (ATRP). The dormant species (the alkoxyamine in NMP or the halo-compound in ATRP) is also the source of radicals. The position of the deactivation–activation equilibria and the 'persistent radical effect' determine the rate of polymerization.[42,43] In RAFT polymerization, the deactivation–activation equilibria are chain-transfer reactions. Radicals are neither formed nor destroyed in these steps and an external source of free radicals is required to initiate and maintain polymerization. Notwithstanding effects of molecular weight and chain length distribution on radical–radical termination and any side reactions (discussed later), the polymerization kinetics should be similar to those found for conventional radical polymerization. Thus the rate of polymerization should be half order with respect to initiator and independent of the RAFT agent. Such behaviour has been demonstrated for MMA polymerization in the presence of dithiobenzoate RAFT agents over an approximate fivefold range of RAFT agent concentrations (0.006–0.03 M) and an approximate 100-fold range of initiator concentrations (0.0005–0.045 M; Fig. 5).[44] Significant retardation of polymerization rate is only evident for the highest concentration of cumyl dithiobenzoate **22**.

Choice of RAFT Agents

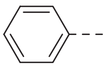
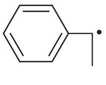
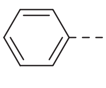
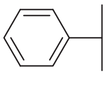
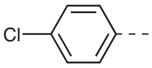
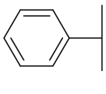
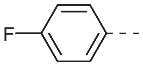
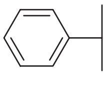
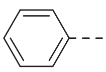
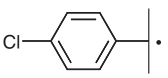
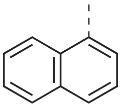
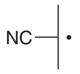
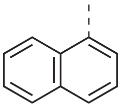
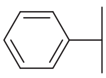
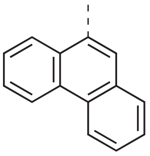
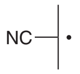
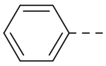
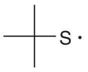
A wide variety of thiocarbonylthio RAFT agents (ZC(=S)SR, **1**) have now been reported. Our initial communication on this form of RAFT polymerization[13] focussed on the utility of dithiobenzoate (Z = Ph) and other dithioesters. However, our patents[14,38,45] and subsequent papers demonstrate that a wide range of thiocarbonylthio compounds can be used. These include certain trithiocarbonates, xanthates, dithiocarbamates, and other compounds. The effectiveness of the RAFT agent depends on the monomer being polymerized and depends strongly on the properties of the free-radical leaving group R and the group Z which can be chosen to activate

Table 2. Aromatic dithioester RAFT agents

RAFT agent	Z	R$^\bullet$	Homopolymers[A–C]	Copolymers[A–D]
6[44]			(MMA),[44] AA[63]	–
7[44]			S,[14,44] (MMA)[6,44]	–
8[9,44]			S,[9,14,44,46] AA,[6] MA,[44,64] MMA,[6,14,44,52] XMA,[65–67] VBz,[13,14] *MMA*,[68] *BMA*,[68] *EHMA*[68]	NIPAM-XMA,[69] S-MAH,[70] *EHMA-b-S*,[68] *EHMA-b-MMA-MA*[68]
9			AN[71]	–
10			SSO$_3$Na,[6,13,14] AMPS[72]	AMPS-AMBS,[72] AMPS-*b*-AMBS[72]
11[44]			MMA[6,13,44]	–
12			S,[6,14] DMAEMA,[13] AM[73]	–
13			AM[73,74]	–
14[44]			(MMA)[44]	–
15		HO$_2$C–$^\bullet$	(S),[14,56] SAc,[75] (MA),[14] BA,[56] (MMA)[56]	–
16		C$_2$H$_5$OC(O)–$^\bullet$	(S),[56] BA,[56] (MMA)[56]	–
17			S,[56] BA,[56] (MMA)[56]	–
18[44]			S,[14,44] (MMA)[14,44]	–
19			BMDO[76]	–
20[44]			S,[14,44,46,77] MA,[44] BA,[13,44] (MMA),[44] DMA,[14] NIPAM,[78] *S*,[9,14] *MMA*[9]	S-*b*-DMA,[14,77] S-*b*-SMe,[14,77] *MMA-b-S*,[9] S-MAH,[51,79,80] (AMS-MAH)[51]

(*continued*)

Table 2. Aromatic dithioester RAFT agents
(*continued*)

RAFT agent	Z	R•	Homopolymers[A–C]	Copolymers[A–D]
21			S,[44,53] AA,[13,14] MA,[14,64,77,81] BA,[9,14,44,77] (MMA),[44] *S*[9,82]	BA-*b*-AA,[14,77] MA-*b*-EA[14,77]
22[9]			S,[6,9,13,14,44,53,55] MA,[44,81,83,84] BA,[9,14] MMA,[13,14,44,52,77] BzMA,[77] DMAEMA,[6] XMA,[65,66] AM,[73] DMA,[6] NIPAM,[6,78] 2VP,[85] 4VP,[85] CPM,[14] (*S*),[9,82] *MMA*,[14] *BMA*[14]	S-AN,[13,14] S-MMA,[14] MMA-HEMA,[13,14] MMA-BA,[5] HEMA-iBMA-MMA-S,[14] MMA-*b*-MAA,[14,77] MMA-*b*-S,[14,77] BzMA-*b*-DMAEMA,[77] BzMA-*b*-MAA,[77] 2VP-*b*-4VP,[85] 4VP-*b*-2VP,[85] *MMA-b-S*,[14] *BMA-b-S*[14]
23			MMA[14]	–
24			MA[81]	–
25[44]			MMA[14,44]	–
26			S,[86] MMA,[87] GMA[88]	MMA-*b*-S[87]
27			MMA[14]	MMA-*b*-S[87]
28			MMA[89]	MMA-*b*-S[89]
29[44]			MMA,[14,44] BA[14,44]	–

[A] If monomer is in parentheses only poor control was reported.

[B] Abbreviations: AA, acrylic acid; AM, acrylamide; AMBS, sodium 3-acrylamido-3-methylbutanoate; AMPS, sodium 2-acrylamido-2-methylpropane-1-sulfonate; AMS, α-methylstyrene; AN, acrylonitrile; BA, butyl acrylate; BAM, *N*-*tert*-butyl acrylamide; BMA, butyl methacrylate; BzMA, benzyl methacrylate; BMDO, 5,6-benzo-2-methylene-1,3-dioxepan; CPM, 2,4,4,6-tetrakis(ethoxycarbonyl)hepta-1,6-diene; DAGMA, diacetone glucose methacrylate; DMA, *N*,*N*-dimethylacrylamide; DMAEMA, *N*,*N*-(dimethylamino)ethyl methacrylate; EA, ethyl acrylate; EHA, 2-ethylhexyl acrylate; EHMA, 2-ethylhexyl methacrylate; GMA, glycidyl methacrylate; HEA, 2-hydroxyethyl acrylate; HEMA, 2-hydroxyethyl methacrylate; iBMA, isobutyl methacrylate; MA, methyl acrylate; MAH, maleic anhydride; MMA, methyl methacrylate; NIPAM, *N*-isopropyl acrylamide; NPMI, *N*-phenylmaleimide; NVP, *N*-vinylpyrrolidone; S, styrene; SAc, 4-acetoxystyrene; SMe, 4-methylstyrene; SSO$_3$Na, sodium styrene-4-sulfonate; tBA, *tert*-butyl acrylate; VAc, vinyl acetate; VBz, vinyl benzoate; VDC, vinylidene chloride; 4VP, 4-vinylpyridine; 2VP, 2-vinylpyridine; XMA, functional methacrylate: 2-(acetoacetoxy)ethyl methacrylate,[66] 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate,[65] 6[4-(4′-methoxyphenyl)phenoxy]hexyl methacrylate,[67] *N*-hydroxysuccinimide methacrylate.[69]

[C] Emulsion or miniemulsion experiments in italics.

[D] For block copolymers, the first polymerized block is mentioned first.

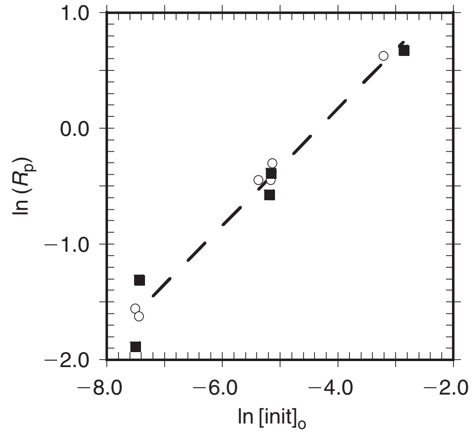


Fig. 5. Plot of log (initial R_p) versus log (initial initiator concentration). Data are for bulk MMA polymerization at 60°C with AIBN initiator (0.0005–0.045 M) and either cumyl dithiobenzoate **22** (■) or 2-cyanoprop-2-yl dithiobenzoate **8** (○) as RAFT agent (0.006–0.03 M). A least-squares fit provides a slope of 0.507, *R* 0.98655.[44]

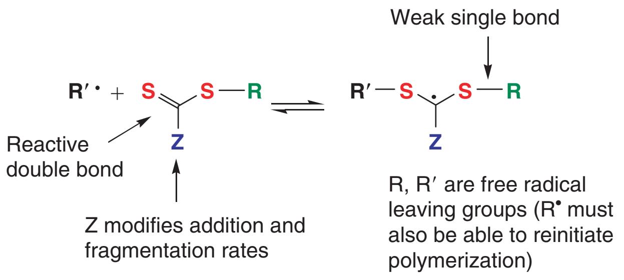


Fig. 6. Structural features of thiocarbonylthio RAFT agent and the intermediate formed on radical addition.

or deactivate the thiocarbonyl double bond and modify the stability of the intermediate radicals (Fig. 6).[6,9,44,46] For an efficient RAFT polymerization (Scheme 6):

- The RAFT agents **1** and **4** should have a reactive C═S double bond (high k_{add}).
- The intermediate radicals **3** and **5** should fragment rapidly (high k_β, weak S—R bond) and give no side reactions.
- The intermediate **3** should partition in favour of products ($k_\beta \geq k_{-add}$).
- The expelled radicals ($R^\bullet$) should efficiently re-initiate polymerization.

A non-exhaustive summary of RAFT agents and the polymerizations in which they have been applied is provided in Tables 2–7. These tables include some RAFT agent/monomer combinations which provide poorer molecular weight control and/or polydispersity >1.4. These are indicated by the monomer being in parentheses. Often these have been investigated in order to provide an understanding of the mechanism and to allow construction of guidelines for the choice of RAFT agent. Fig. 7 provides a summary of how to select the appropriate RAFT agent for particular monomers.

Several papers have been published on the effects of the substituents R and Z on the effectiveness and transfer coefficients of RAFT agents.[6,9,44,46] The rate of addition of radicals to the C═S double bond is strongly influenced by the substituent Z. This rate is higher when Z = aryl, alkyl (dithioesters), or *S*-alkyl (trithiocarbonates), and lower when Z = *O*-alkyl (xanthates) or *N*,*N*-dialkyl (dithiocarbamates).

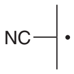
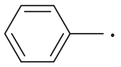
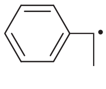
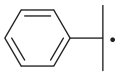
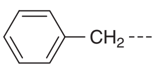
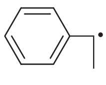
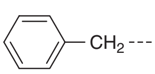
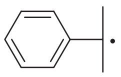
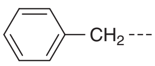
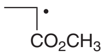
We performed a series of styrene polymerizations (110°C, thermal initiation) for two series of RAFT agents which differ in the activating group Z [S═C(Z)S—CH_2Ph and S═C(Z)S—$C(Me)_2CN$].[46] The chain transfer coefficients were found to decrease as shown in Fig. 7. Only the first five in this series provide narrow-polydispersity polystyrene (<1.2). More generally, chain-transfer coefficients decrease in the series dithiobenzoates > trithiocarbonates ≈ dithioalkanoates > dithiocarbonates (xanthates) > dithiocarbamates. The relatively low activity of *O*-alkyl xanthates and *N*,*N*-dialkyl dithiocarbamate derivatives can be qualitatively understood in terms of the importance of the zwitterionic canonical forms (Scheme 7), which arise through interaction between the O or N lone pairs and the C═S double bond. Electron-withdrawing substituents on Z can enhance the activity of RAFT agents to modify the above order.[38,46–49] Thus, xanthate and dithiocarbamate RAFT agents where the oxygen or nitrogen lone pair is less available for delocalization with the C═S by virtue of being part of an aromatic ring or by possessing an adjacent electron-withdrawing substituent are substantially more effective. For examples see Table 6 (xanthates) or Table 4 (dithiocarbamates). The trend in relative effectiveness of RAFT agents with varying Z is rationalized in terms of interaction of Z with the C═S double bond to activate or deactivate that group towards free-radical addition.

For ring-substituted cyanoisopropyl dithiobenzoate RAFT agents in MMA polymerization, electron-withdrawing groups, which render the thiocarbonyl sulfur more electrophilic, enhance the rate of addition to the C═S double bond and provide narrower polydispersities from the early stages of polymerization (Fig. 8).[50] The opposite is true for electron-donating substituents. Cyanoisopropyl 2,5-dimethyldithiobenzoate gives poor control which is attributed to the *ortho*-substituents sterically inhibiting conjugation of the aromatic ring with the C═S double bond.

For fragmentation to occur efficiently in the desired direction, the substituent R must be a good homolytic leaving group, relative to the attacking radical $P_n^\bullet$. For example, the RAFT agent where R = CH_2Ph (e.g. benzyl dithiobenzoate **20**) functions as a suitable chain-transfer agent in polymerization with styryl and acrylyl propagating radicals but not in those with methacrylyl propagating radical. The benzyl radical is a reasonable leaving group with respect to the styryl and acrylyl propagating radicals but is a poor leaving group with respect to the methacrylyl propagating radical. In MMA polymerization, RAFT agents such as benzyl dithiobenzoate can appear almost inert because R is a poor leaving group with respect to the PMMA propagating radical.[44] The poor control seen with benzyl dithiobenzoate in α-methylstyrene copolymerizations probably has a similar explanation.[51]

The rate of fragmentation of intermediate **3** is enhanced by increasing steric hindrance, by the presence of electron-withdrawing groups, and by radical-stabilizing groups on R.

Table 3. Aliphatic dithioester RAFT agents

RAFT agent	Z	R	Homopolymers[A]	Copolymers[A]
30[46]	H_3C--		S,[46] BA[13]	–
31[46]	H_3C--		S,[14,46] BA,[9] *S*[9,14]	*S-b-MMA*[9,14]
32	H_3C--		S[53]	–
33	H_3C--		MMA[6,52]	–
34			S,[82] MA,[84,90] NIPAM,[91] *S*,[82]	NIPAM-*b*-S[91]
35			S,[54] (MMA),[54] MA,[84] AM,[73] NIPAM[91]	NIPAM-*b*-S[91]
36			MA[92]	–

[A] See footnotes A–D in Table 2.

The suggestion that R might be selected to be a monomeric analogue of the propagating radical is flawed since penultimate unit effects can be substantial, particularly when R is tertiary. Thus, RAFT agent **18** (R = 2-ethoxycarbonylprop-2-yl), where R may be considered as a monomeric propagating radical, is a poor RAFT agent in the polymerization of MMA and other methacrylates because R is a poor leaving group with respect to the PMMA propagating radical.[44] Analogous behaviour is observed for macromonomer RAFT agents.[25,26] For similar reasons, RAFT agent **6** (R = *t*-butyl) is poor with respect to RAFT agent **7** (R = *t*-octyl).[44] These differences in RAFT agent activity are attributed to steric factors. During chain extension, the attacking and leaving propagating radicals ($P_n^\bullet$ and $P_m^\bullet$, n, $m > 2$) are, in essence, identical in all respects other than chain length, and therefore should have equivalent rates in addition to RAFT agent, fragmentation, and propagation. When R is secondary, penultimate unit effects on addition and fragmentation reactions are likely to be smaller but still should not be ignored.

The leaving ability of the substituent R must also be balanced with the ability of the radical $R^\bullet$ to re-initiate polymerization. The triphenylmethyl radical, for instance, would be an excellent leaving group but would be a poor re-initiator of chains and its use would result in retardation of polymerization. For similar reasons, one should also not choose benzylic species (cumyl, 1-phenylethyl, benzyl) for vinyl monomer (VAc) polymerization, since rate of re-initiation would be very low.

In many studies, the effectiveness of RAFT agents has been estimated qualitatively by observing the correspondence between found and calculated molecular weights and the narrowness of the molecular weight distribution. A lesser number of papers have made an attempt to evaluate the transfer coefficients of the RAFT agents or the individual rate constants for addition and fragmentation. In this context, the methods used for determining the transfer coefficients of RAFT agents deserve mention. Conventional methods such as the Mayo method should not be used in the case of the more active RAFT agents. The Mayo method is difficult to apply when transfer coefficients are high. The reversibility of chain transfer means that apparent chain-transfer coefficients are dependent on the transfer agent concentration and on conversion of monomer and the transfer agent. One of the ways of estimating the transfer coefficient is to determine the rates of consumption of RAFT agent and monomer. In the case of RAFT polymerization, it can be shown that the rate of consumption of the transfer agent depends on two transfer coefficients, C_{tr} ($= k_{tr}/k_p$) and $C_{\text{-}tr}$ ($= k_{\text{-}tr}/k_i$), which describe the reactivity of the propagating radical ($P_n^\bullet$), and the expelled radical ($R^\bullet$) respectively (see Eqn 2).[44,46,52]

$$\frac{d[\mathbf{1}]}{d[M]} \approx C_{tr}\frac{[\mathbf{1}]}{[M] + C_{tr}[\mathbf{1}] + C_{\text{-}tr}[\mathbf{4}]} \tag{2}$$

Note that in chain transfer by addition–fragmentation (Scheme 6), the rate coefficient for chain transfer (k_{tr}) is given by Eqn 3:

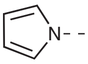
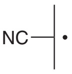
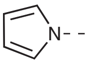
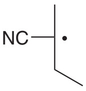
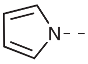
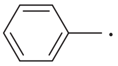
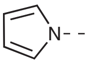
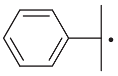
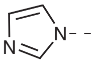
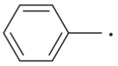
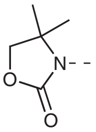
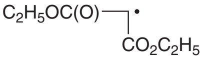
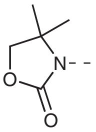
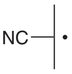
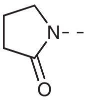
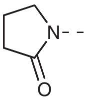
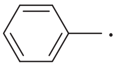
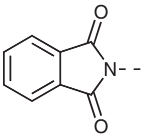
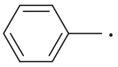
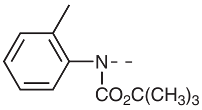
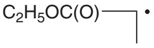
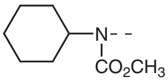
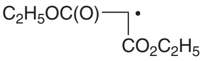
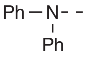
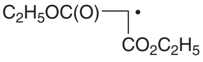
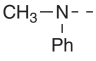
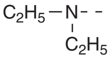
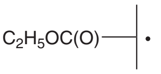
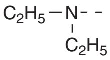
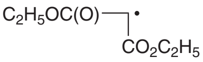
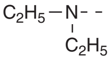
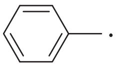
$$k_{tr} = k_{add} \times \frac{k_\beta}{k_{\text{-}add} + k_\beta} \tag{3}$$

We similarly define $k_{\text{-}tr}$ as shown in Eqn 4.

$$k_{\text{-}tr} = k_{\text{-}\beta} \times \frac{k_{\text{-}add}}{k_{\text{-}add} + k_\beta} \tag{4}$$

These relationships (Eqns 2–4) are derived by application of a steady-state approximation and assume that the adduct radical **3** undergoes no reactions other than fragmentation. Eqn 2 can be solved numerically to estimate transfer

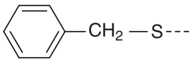
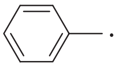
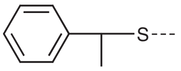
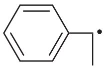
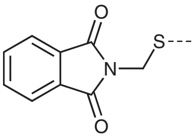
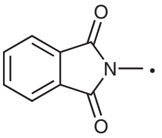
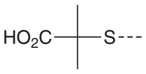
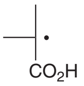
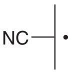
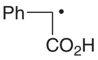
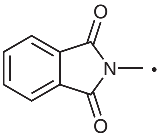
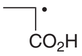
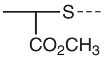
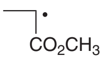
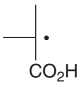
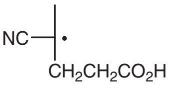
Table 4. Dithiocarbamate RAFT agents

RAFT agent	Z	R	Homopolymers[A]	Copolymers[A]
37[46]			S,[46] MA,[38] MMA[38,47]	–
38			MMA[38]	–
39[46]			S,[6,38,46,47] MA,[6,38,47] NIPAM[93]	–
40			NIPAM[93]	–
41			S,[47] MA[38,47]	–
42			EA[48]	–
43			S,[48] (MMA),[48] VAc[48]	–
44			AN,[B] MA[B]	AA-*b*-NIPAM[94,95]
45[46]			(S),[38,46] MA[38]	–
46			S,[38] (MA)[38]	–
47			EA[48]	–
48			S,[48] EA,[48] VAc[48]	–
49	 $\mathrm{Ph-\underset{Ph}{N}-\,-}$		EA,[48] (VAc)[48]	–
50	 $\mathrm{CH_3-\underset{Ph}{N}-\,-}$	NC–•	VAc[6]B	–
51	 $\mathrm{C_2H_5-\underset{C_2H_5}{N}-\,-}$		VAc[6]	–
52	 $\mathrm{C_2H_5-\underset{C_2H_5}{N}-\,-}$		(EA),[48] (VAc)[48]	–
53[46]	 $\mathrm{C_2H_5-\underset{C_2H_5}{N}-\,-}$		(S)[6,46]	–

[A] See footnotes A,B,D in Table 2.

[B] See Table 9.

Table 5. Trithiocarbonate RAFT agents

RAFT agent	Z	R	Homopolymers[A]	Copolymers[A]
54			S,[14,46,96] AA,[63,97] MA[96]	S-MAH[98]
55			S[96]	–
56			S[15]	–
57			S,[99] AA,[99] HEA,[99] EA,[99] BA,[99,100] (MMA),[99] AM[73]	AA-*b*-EA, S-*b*-AA, EHA-*b*-EA[99]
58[46]	H_3C–S---		S,[6,46,96] MA,[6,96] MMA[6,96]	–
59	H_3C–S---		S[6,96]	–
60	C_4H_9–S---		S,[15,101] BA[101]	–
61	C_4H_9–S---		AA[102,103]	*AA-b-S*,[102] *AA-b-BA*[102,103]
62			MA[92]	–
63	$CH_3(CH_2)_{11}$–S---		AA,[99] EA,[99] BA,[100] BAM,[99] NIPAM[104]	AA-*b*-EA, AA-*b*-S[99]
64	$CH_3(CH_2)_{11}$–S---		MMA[15]	–

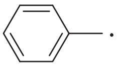
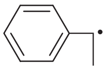
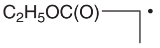
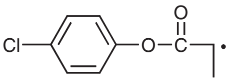
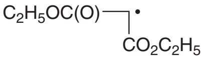
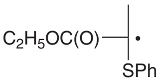
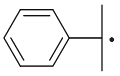
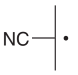
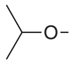
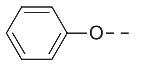
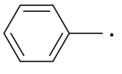
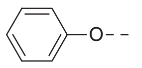
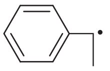
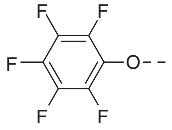
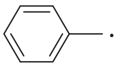
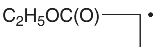
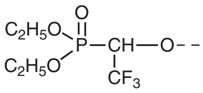
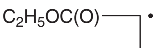
[A] See footnotes A–D in Table 2.

coefficients.[46,52] Transfer coefficients in RAFT polymerization can also be estimated by analyzing the dependence of the molecular-weight distribution on monomer/RAFT agent conversion.[43,46,53–55] We have shown[46] apparent transfer constants determined with neglect of the back reaction of R$^\bullet$ with RAFT agent (i.e. by assuming $C_{\text{-tr}} = 0$) can underestimate the actual transfer constant by more than an order of magnitude in the case of the more active RAFT agents.

The dependence of RAFT agent activity on the substituents R and Z can be qualitatively predicted using low-level molecular orbital calculations, and these also provide a guide to the relative importance of the various factors.[44,46,56] There also appear to be good prospects for more quantitative predictions using high-level ab initio calculations.[46,50,57–62] These studies are able to predict dependence of RAFT agent activity on the Z and R substituents and, by providing some understanding of the reason for this dependence, may prove extremely useful in RAFT agent design. However, this work is still in its infancy, and the use of these methods to predict absolute values of rate constants or equilibrium constants associated with RAFT must still be treated with caution.

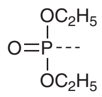
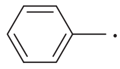
Even though there is a large range of potential RAFT agents, it should be stated that a majority of polymerizations could be conducted with just two RAFT agents (Fig. 7); one suited to (meth)acrylate, (meth)acrylamide, and styrenic monomers, for example, a tertiary cyanoalkyl trithiocarbonate, and another suited to vinyl monomers such as VAc, for example, a cyanoalkyl xanthate. Ease of preparation, compatibility with reaction media, desired end-group functionality, and polymer architecture might, however, dictate the use of other RAFT agents. In these circumstances, Fig. 7 will

Table 6. Xanthate RAFT agents

RAFT agent	Z[A]	R	Homopolymers[B]	Copolymers[B]
65	C_2H_5–O--	NC–•	VAc[6][C]	MA-VAc[D]
66	C_2H_5–O--		(S),[46] (*S*)[9]	–
67	C_2H_5–O--		(S),[16,105–107] (BA),[38] (*S*)[9]	–
68[D]	C_2H_5–O--		(S),[16,49,106,107] AA,[108] (MA),[16] (EA),[16,49] AM,[108] VAc,[6,16] (*S*),[16] (*BA*)[16]	AA-AM,[108] AA-*b*-AM,[108] AA-AM-*b*-AM[108]
69	C_2H_5–O--		(S)[106]	–
70	C_2H_5–O--		(S)[16,106]	–
71	C_2H_5–O--		(S),[16,106] (EA)[16]	–
72	C_2H_5–O--		(S)[106]	–
73	C_2H_5–O--		(S),[106] (tBA),[6] (MMA)[38]	–
74		$CH_3OC(O)$–•	VAc[109]	–
75[46]			(S),[46] (AA)[63]	–
76[46]			AA[63]	–
77[46]			(S),[46] (tBA)[38]	tBA-VAc[38,110]
78	CF_3CH_2–O--		(S),[49,107] EA[49]	–
79			S,[49] EA[49]	–

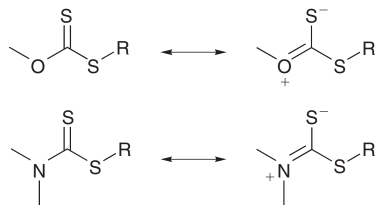
[A] Some entries relate to methyl rather than ethyl ester. [B] See footnotes A–D in Table 2. [C] See Table 9. [D] See Table 10.

Table 7. Other RAFT agent

RAFT agent	Z	R	Homopolymer[A]	Copolymer
80			S[14,111,112]	–

[A] See footnote B to Table 2.

provide some guidance. For example, in RAFT polymerization of a methacrylate, one should choose a RAFT agent with the Z group from aryl, *S*-alkyl, or pyrrole and the R group from tertiary cyanoalkyl or cumyl.



Scheme 7. Canonical forms of xanthates and dithiocarbamates.

Synthesis of RAFT Agents

Currently, few RAFT agents are commercially available. However, RAFT agents are available in moderate-to-excellent yields by a variety of methods, and syntheses are generally straightforward.

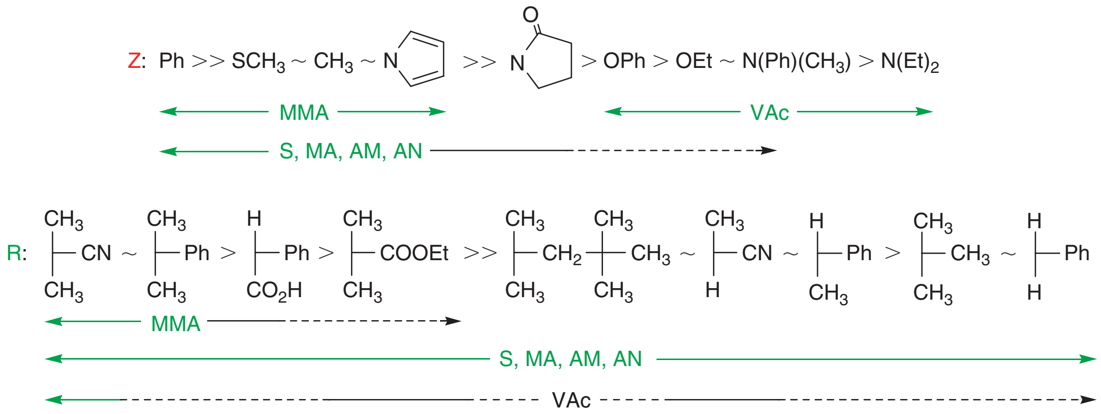


Fig. 7. Guidelines for selection of RAFT agents for various polymerizations. For Z, addition rates decrease and fragmentation rates increase from left to right. For R, fragmentation rates decrease from left to right. Dashed line indicates partial control (i.e. control of molecular weight but poor polydispersity or substantial retardation in the case of VAc). For monomer abbreviations see footnotes to Table 2.

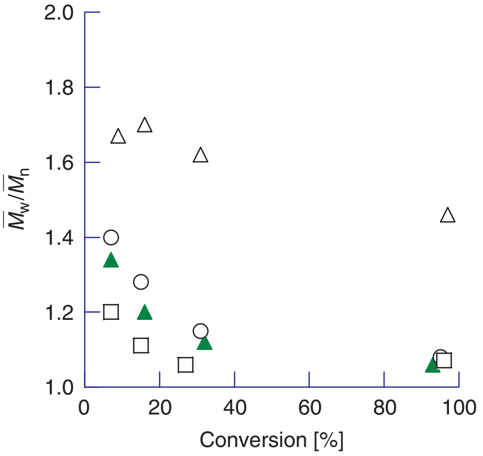
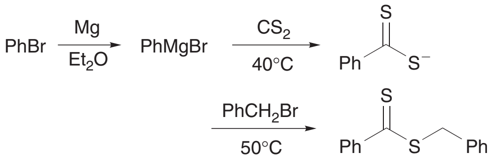
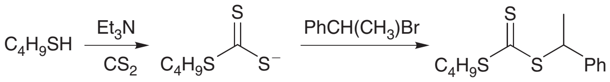


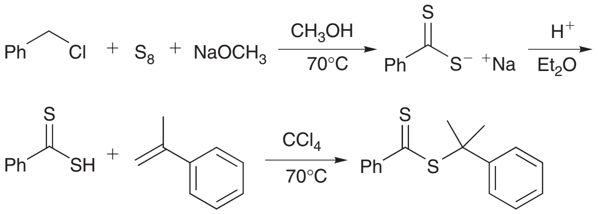
Fig. 8. Evolution of polydispersity with conversion for MMA polymerizations carried out with ring-substituted cyanoisopropyl dithiobenzoate RAFT agents 2,5-dimethyldithiobenzoate (△), 4-methoxydithiobenzoate (○), dithiobenzoate (▲), and 2,5-di(trifluoromethyl)dithiobenzoate (□).[50]



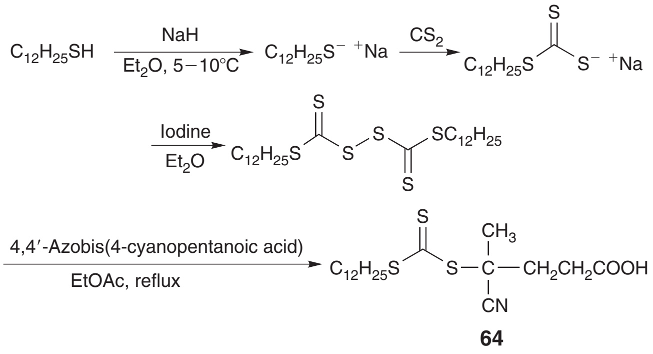
Scheme 8.



Scheme 9.



Scheme 10.



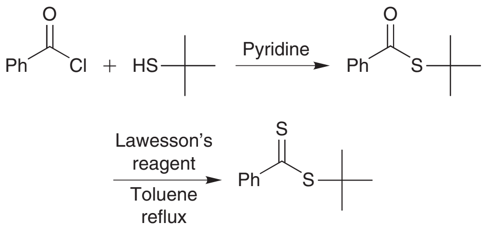
Scheme 11.

Some of the methods exploited in recent work include:

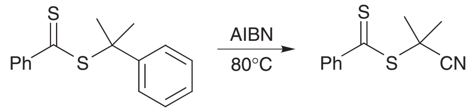
- Reaction of a carbodithioate salt with an alkylating agent (Scheme 8).[14,44,46,56,113] Often this will involve sequential treatment of an anionic species with carbon disulfide and an alkylating agent in a one-pot reaction. For example, we have used this process to prepare benzyl dithiobenzoate,[46] 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate,[46] and 2-cyanoprop-2-yl dithiobenzoate.[9] Similar chemistry is used in the synthesis of unsymmetrical trithiocarbonates (Scheme 9).[114,115] Yields are generally high (>70%) for substitution of primary and secondary alkyl halides, but can be low for tertiary halides (5–40%).
- Addition of a dithio acid across an olefinic double bond.[44,116,117] This procedure has been used to prepare cumyl dithiobenzoate (Scheme 10).[9,14] Electron-rich olefins (S, AMS, isooctene, VAc) give Markownikov addition (sulfur at substituted position) and useful RAFT agents, while electron-deficient olefins (MMA, MA, AN) unfortunately give Michael-like addition (sulfur at unsubstituted position).
- Radical-induced decomposition of a bis(thioacyl) disulfide (e.g. Scheme 11).[15,45,46,118,119] This is probably the most used method for the synthesis of RAFT agents requiring

tertiary R groups. It is also possible to use this chemistry to generate a RAFT agent in situ during polymerization.[45]

- Sulfuration of a thioloester,[14,44] a carboxylic acid plus an alcohol[120] or a carboxylic acid with a halide or olefin[121] with P_4S_{10}, or Davey or Lawesson's reagent (Scheme 12).
- Radical-induced ester exchange.[9,44,46,122] For this method to be effective, the R group of the precursor RAFT agent should be a good free-radical leaving group with respect to that of the product RAFT agent. For example, the cyanoisopropyl radical generated from azobis(isobutyronitrile) (AIBN) can replace the cumyl group of cumyl dithiobenzoate (Scheme 13).[9]



Scheme 12.



Scheme 13.

In the synthesis of dithiobenzoates (and related dithioesters) by the above processes, either dithiobenzoic acid or its salts will often be formed in situ by various routes. These include the reaction of benzyl chloride[9,123] or a benzyl sulfone[124] with elemental sulfur in the presence of base, reaction of phenyl Grignard reagent with carbon disulfide,[9] and treatment of benzoic acid with P_4S_{10} or Davey reagent.[121,125]

Evidence in Support of the RAFT Mechanism

Evidence in support of the overall RAFT reaction (Scheme 4) is the retention of the RAFT end groups; this can be demonstrated by NMR spectroscopy and mass spectrometry. Many papers on RAFT provide NMR spectra of RAFT-made polymers. Fig. 9 shows the expected structure and the ^{1}H NMR spectrum of a PMMA of $\overline{M}_n = 2600$ and $\overline{M}_w/\overline{M}_n = 1.17$ prepared by the solution polymerization of methyl methacrylate at 90°C in benzene in the presence of RAFT agent **64** (sealed tube). The end groups of the polymer are clearly visible in the spectrum and give different signals to those observed in the ^{1}H NMR spectrum of the RAFT agent.

Additional evidence for the retention of the RAFT end groups and the quality of RAFT polymerization under various conditions is provided by matrix-assisted laser desorption ionization time-of-flight (MALDI–TOF) or electrospray ionization (ESI) mass spectrometry. Systems studied by mass spectrometry include (polymer/RAFT agents): PNIPAM/**20**,**22**,[78] PNIPAM/**39**,**40**,[93]

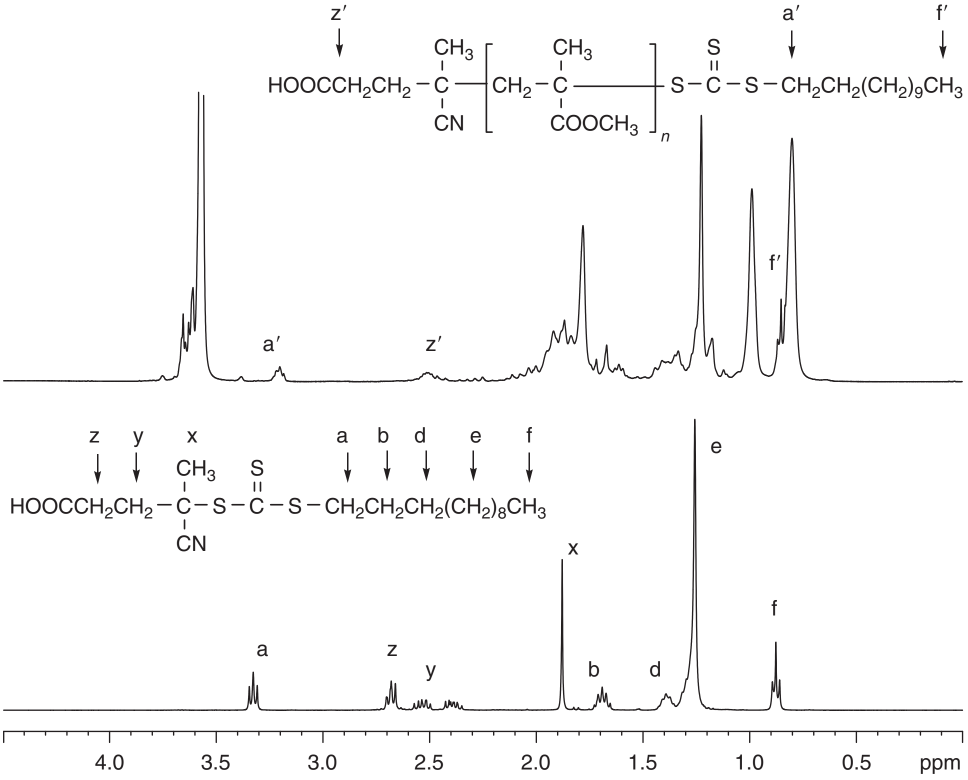


Fig. 9. Structure and ^{1}H NMR spectra (400 MHz, $CDCl_3$) of *S*-dodecyl *S*-(2-cyano-4-carboxy)but-2-yl trithiocarbonate **64** (bottom) and a poly(methyl methacrylate) (top) prepared in its presence. The NMR spectra show that the RAFT agent **64** is absent from the polymer product. However, signals associated with the two end groups can be observed.

PVAc/**49**,[48] PS/**21**,[126] PS/**69**,[106] PMMA/**8**,**11**,[100] PBA/**57**,**63**,[127] PMA/**21**,**22**,**24**,[81,83] PEA/**79**,[49] and poly-(acenaphthalene)/**81**.[128] ESI is a softer ionization technique than MALDI–TOF and is more likely to leave the end groups intact to be observed in the mass spectrum.[100,129] MALDI–TOF analysis was successfully carried out on the poly(acenaphthalene) **82** prepared with RAFT agent **81**.[128] The major peaks in the spectrum (Fig. 10) correspond to: $m_{81} + nm_{\mathrm{AcN}} + m_{\mathrm{Ag}} = (153 + 316) + (152n) + 108$; consistent with the polymer being capped with PhC(=S)S and anthracenyl moieties as expected for structure **82**.

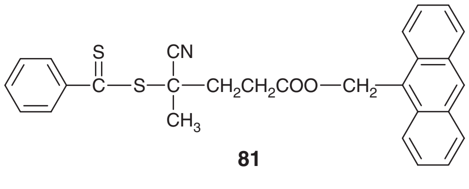
Interaction chromatography (liquid chromatography at the critical point of adsorption; LC-CC) and two-dimensional chromatography (2D GPC/LC-CC) have also been applied to establish the presence of RAFT end groups and the quality of RAFT polymerization. Pasch et al.[130] used 2D GPC/LC-CC to examine a PMMA-*b*-PS prepared in our laboratories by RAFT with cumyl dithiobenzoate as the RAFT agent and were able to 'confirm the remarkable molar mass and compositional homogeneity' of the sample. Jiang et al. have determined the end-group composition (fraction of RAFT agent and initiator-derived chain ends) of PMMA[100] and PBA[127] prepared by RAFT with functional RAFT agents by LC-CC coupled with mass spectrometry.

We obtained the electron paramagnetic resonance (EPR) spectrum of intermediate radical **83** shown in Fig. 11 during BA polymerization at 90°C with cumyl dithiobenzoate **22** as RAFT agent.[131] This provided the first direct evidence for the addition–fragmentation mechanism and the involvement of species such as **3** and/or **5** as discrete intermediates (Scheme 6). The intermediates have been observed directly by EPR in RAFT polymerizations of styrene and acrylate esters and in model reactions with dithiobenzoate and dithiophosphonate RAFT agents.[112,131–136] The intermediates **3** or **5** are not detectable during MMA polymerizations or in polymerizations with aliphatic dithioester, trithiocarbonate, xanthate, or dithiocarbamate RAFT agents. This is attributed to the greater rate of fragmentation and the correspondingly shorter lifetime of the adduct in these polymerizations.

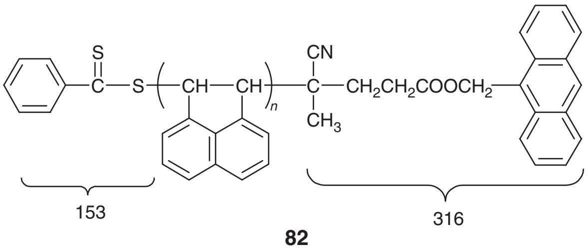
Side Reactions in RAFT

A variety of side reactions can potentially complicate the RAFT mechanism causing retardation, by-products, and anomalies in the molecular-weight distributions.[137] Whether these occur depends on the particular RAFT agent/monomer combination and the reaction conditions.

Retardation is observed in RAFT polymerizations when high concentrations of RAFT agent are used and/or an inappropriate choice of RAFT agent is made. Some decrease in polymerization rate is clearly attributable to a mitigation of the gel (or Trommsdorf) effect.[44,46] However, it is also clear that other effects are important in some circumstances.



81



82

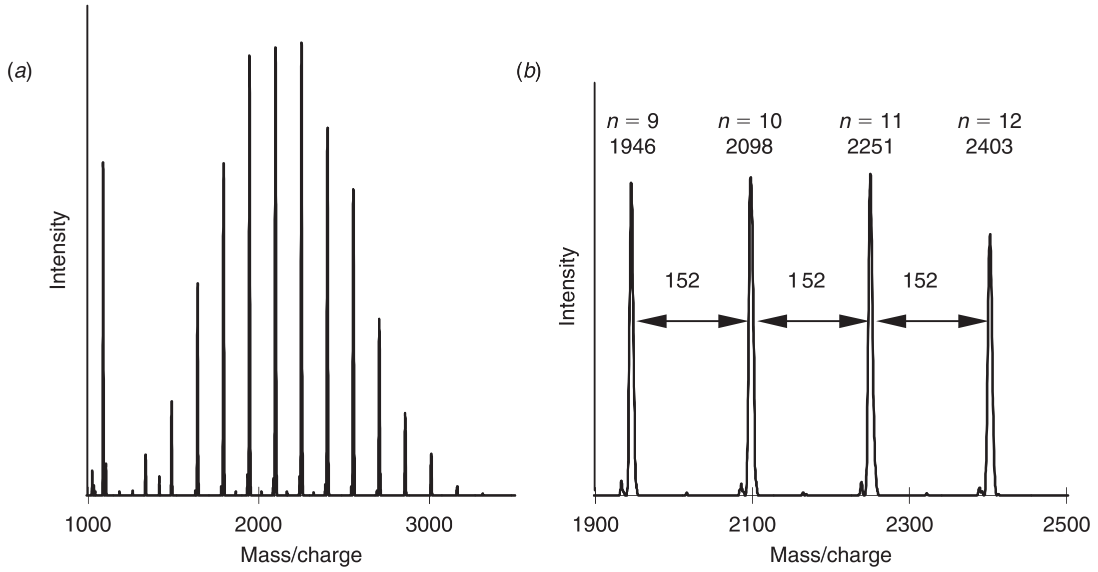
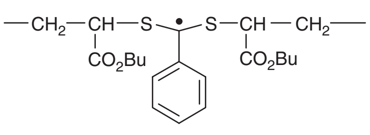


Fig. 10. (*a*) MALDI–TOF mass spectrum of **82** (dithranol as matrix; silver trifluoroacetate as cationizing agent, chloroform as solvent); and (*b*) expanded region of spectrum.[128] The peaks are labelled with their measured molecular weights and the number of repeating units (*n*). The interpeak distances correspond to the mass of the acenapthalene repeat unit.



83

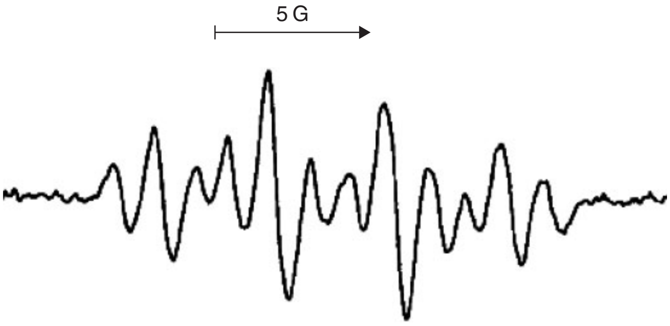


Fig. 11. EPR spectrum observed during the polymerization of *n*-butyl acrylate with dimethyl 2,2′-azobisisobutyrate (AIBMe) initiator and cumyl dithiobenzoate **22** at 90°C at 4 min [α_H/G 3.66 (2H, *ortho*); 1.41 (2H, *meta*), 3.96 (1H, *para*), 0.28 (2H, γH)].[131] The polymerization mixture comprised AIBMe (10.5 mg, 4.56×10^{-5} mol) and **22** (28.6 mg, 1.05×10^{-4} mol) in benzene (0.5 mL) and butyl acrylate (0.5 mL).

For example, there is significant retardation in the polymerization of acrylate esters in the presence of dithiobenzoate esters.[9,44,52,64,84,136–138] For polymerization of MA with benzyl **20** or cyanoisopropyl dithiobenzoate **8** as RAFT agent at 60°C, we found retardation from the onset of polymerization. The retardation appeared not to be directly related to consumption of the initial RAFT agent (which was rapid), with the dithioester being completely consumed at the first time/conversion point. An aliphatic dithioester, benzyl dithioacetate **31**, was found to give substantially less retardation under the same reaction conditions (Fig. 12). The observation of less retardation in RAFT polymerization of acrylate esters with aliphatic dithioesters and trithiocarbonate RAFT agents than is seen with dithiobenzoate RAFT agents has also been reported under other circumstances.[9,52,64,84,137] Quinn et al.[90] observed that 1-phenylethyl dithiophenylacetate **34** enabled RAFT polymerization of MA at ambient temperature, whereas 1-phenylethyl dithiobenzoate **21** strongly retarded polymerization under the same conditions. McLeary et al.[84] observed that RAFT polymerization of MA with cumyl dithiophenylacetate **35** was subject to an inhibition period corresponding to the consumption of the initial RAFT agent. This was attributed to slow re-initiation by the cumyl radical during what was called the initialization period. Available data indicate that the rate constant for addition of cumyl radicals to MA is slow with respect to that for propagation.[44,139] The reported rate constants for benzyl and cyanoisopropyl radicals adding to MA is similarly slow or slower with respect to propagation, yet no substantial inhibition period is seen with these RAFT agents.[44,139] We propose that the inhibition period relates not to slow re-initiation by cumyl radical in itself, rather to the importance of the back reaction of cumyl radicals with the RAFT agent.[44] Cumyl radicals add to RAFT agents at close to diffusion controlled rates which has the effect of magnifying any problems associated with slow re-initiation and also leads to concentration dependence of the apparent transfer constants. This is also a known issue in MMA and styrene polymerization with cumyl dithiobenzoate (see below).[44]

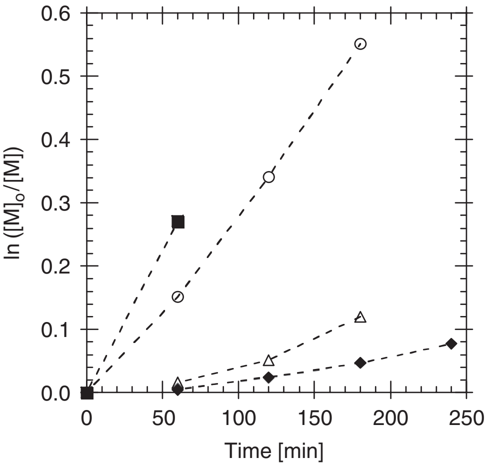
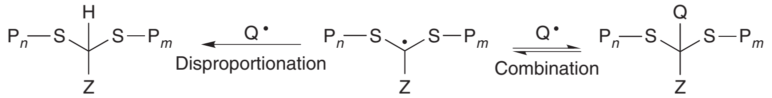


Fig. 12. Pseudo first-order rate plot for bulk polymerization of MA (4.45 M in benzene) at 60°C with approx. 3.3×10^{-4} M AIBN in the absence (■) or presence (○) of MeC(=S)CH$_2$Ph **31** (0.00306 M); **31** (0.0306 M) (△); PhC(=S)SCH$_2$Ph **20** and PhC(=S)SC(Me)$_2$CN **8** (0.00366 M) (◆). The plots for **8** and **20** are superimposed.[137]

Retardation has also been observed in polymerizations of styrene and methacrylates, and is pronounced when high concentrations of dithiobenzoate RAFT agents are used.[9,52–55,133,137,140,141] With lower concentrations of RAFT agents such as cyanoisopropyl dithiobenzoate **8** and cumyl dithiobenzoate **22** (<0.03 M), we have shown that rates of polymerization for styrene and MMA are little different from that expected in the absence of RAFT agent and appear independent of the particular dithiobenzoate.[9,44,52] Inconsistencies in reported rates of polymerization suggest that, in some cases, lower rates may in part be attributed to extraneous factors such as impurities in the RAFT agent or incomplete degassing. For higher RAFT agent concentrations, the extent of retardation becomes markedly dependent on which initial RAFT agent is used and its concentration. Much less retardation is seen with cyanoisopropyl dithiobenzoate **8** than is seen with cumyl dithiobenzoate **22**. The retardation is in part manifested as an inhibition period which corresponds to the time taken to convert that RAFT agent into the polymeric RAFT agent. The apparent transfer constant measured by the rate of utilization of the RAFT agent is strongly concentration dependent.[9,44,52]

There is currently some controversy surrounding the stability and possible alternate fates of the intermediate radical



Scheme 14.

Table 8. RAFT polymerization of unpurified commercial MMA with RAFT agent 64 under various conditions[A]

Atmosphere	Time [h]	Conversion [%]	$\overline{M}_n$[B]	$\overline{M}_w/\overline{M}_n$
Freeze-evacuate	1.5	93	100000	1.25
N_2 flush	1.5	87	90000	1.25
In air[C]	1.5	26	38000	1.38
In air[C]	3.0	88	112000	1.26

[A] Polymerization of 10 g MMA with 20 mg of RAFT agent **64** and 5 mg of AIBN at 80°C for the times indicated.
[B] GPC molecular weight in polystyrene equivalents.
[C] No degassing.

in RAFT polymerization. These adducts might, in principle, undergo various side reactions. They include:

- Reaction of the intermediate radicals **3** or **5** with other radical species such as an initiator-derived or a propagating radical.[140] In the case of **5**, coupling with a propagating radical leads to a three-armed star (Scheme 14).[53,126,133,141]
- Reaction of the intermediate radicals **3** or **5** with another such radical. In the case of self-reaction of **5**, this pathway leads to a four-armed star.
- Reaction with oxygen and impurities. RAFT polymerization can show sensitivity to air and impurities in the monomer. Results for polymerizations carried out with unpurified commercial MMA at 80°C with thorough degassing by freeze–evacuate–thaw cycles, a simple nitrogen flush, and no degassing are shown in Table 8. All polymerizations provide narrow molecular-weight distributions and some molecular weight control. However, polymerizations with no degassing give substantial retardation. All polymerizations yield a lower-than-expected molecular weight which we attribute to the use of unpurified monomer.
- For some RAFT agents there are multiple pathways for β-scission involving cleavage of a bond within the 'Z'-group. For unsymmetrical trithiocarbonates[96] and xanthates[57] two possible fragmentation pathways are possible.
- Reaction with monomer to re-initiate polymerization. Copolymerization of macromonomer RAFT agents has been observed;[32] however, the pathway is currently unknown for thiocarbonylthio RAFT agents.

Slow fragmentation, by itself, is an unlikely cause for retardation in RAFT polymerization of styrene and methacrylates. This would require that the rate of fragmentation be very low and that the concentrations of the adduct radicals **3** or **5** be very high (approx. 10^{-4} M for styrene polymerization with cumyl dithiobenzoate); much higher than is observed experimentally by EPR ($<10^{-7}$ M).[131] However, the adduct radical formed by addition to dithiobenzoate RAFT agents should be significantly more stable than that formed by addition to aliphatic dithioesters or trithiocarbonates. This expectation is supported by molecular orbital calculations.[58] Slower fragmentation should then mean that this radical is more likely to be involved in side reactions such as coupling with radical species. There is currently vigorous debate with respect to the significance of coupling reactions involving the adduct radicals **3** or **5** during polymerization. For dithiobenzoate RAFT agents, the pathway has been observed with model systems under conditions of high radical flux.[126,133,140,141] However, there is as yet no direct evidence that the process occurs during polymerization even under conditions where significant retardation is observed. We have proposed that inhibition in vinyl acetate polymerization is caused by side reactions of the adduct radical.[6]

Initiation and Termination in RAFT Polymerization

Since radicals are neither formed nor destroyed during reversible chain transfer, RAFT polymerization must be initiated by a source of free radicals. RAFT polymerization is usually carried out with conventional radical initiators. In principle, any source of free radicals can be used,[14] but most often thermal initiators (e.g. AIBN, ACP, $K_2S_2O_8$) are used. Styrene polymerization may be initiated thermally between 100 and 120°C. Polymerizations initiated with UV irradiation,[142,143] a γ-source,[144–149] or a plasma field[150] have been reported. In these polymerizations, radicals may be generated directly from the RAFT agent and these may be responsible for initiation. It was suggested by Pan and coworkers that the mechanism for molecular weight control in UV[143] and γ-initiated[147] processes might involve reversible coupling and be similar to that proposed by Otsu et al.[151] to describe the chemistry of dithiocarbamate photoiniferters. However, Quinn et al.[142,145] have demonstrated that the living behaviour observed in these polymerizations can be attributed to the standard RAFT mechanism (Scheme 6).

The initiator concentration and rate of radical generation in RAFT polymerization are chosen to provide a balance between an acceptable rate of polymerization and an acceptable level of dead chains (radical–radical termination). One useful guideline is to choose conditions so that the target molecular weight is about 10% of that which would have been obtained in the absence of RAFT agent. One common misconception is that it is necessary to use very low rates of polymerization in order to achieve narrow molecular weight distributions. Sometimes, using a high rate of polymerization and a correspondingly short reaction time can provide better results. It is very important not to use prolonged reaction times when retention of the RAFT functionality is important.

Once the monomer is fully converted, continued radical generation may not change the molecular weight distribution, but it can lead to formation of dead chains.

Side reactions of the initiator or initiator-derived radicals with the RAFT agent are possible. However, these are not always readily discernable because of the high RAFT agent-to-initiator ratios used in well designed experiments. It follows from the mechanism of the RAFT process that there should be a fraction of dead chains formed relating directly to the number of chains initiated. Ideally, this fraction should be taken into account when calculating the molecular weights of polymers formed by the RAFT process.[44] The molecular weight of the polymer formed can be estimated knowing the concentration of the monomer consumed and the initial concentration of RAFT agent by using the simple relationship shown in Eqn 1. Positive deviations from Eqn 1 indicate incomplete usage of RAFT agent. Negative deviations indicate that other sources of polymer chains are significant. These include the initiator-derived chains.

If initiator-derived chains are significant, Eqn 5 should be used to calculate molecular weights:

$$\overline{M}_n(\text{calc.}) = \frac{[\mathrm{M}]_o - [\mathrm{M}]_t}{[\mathbf{1}]_o + df([\mathrm{I}]_o - [\mathrm{I}]_t)} m_\mathrm{M} + m_\mathrm{RAFT} \qquad (5)$$

where m_M and m_RAFT are molecular weights of the monomer and the RAFT agent respectively, d is the number of chains produced from radical–radical termination ($d \approx 1.67$ in MMA and $d \approx 1.0$ in styrene polymerization), $[\mathrm{I}]_o - [\mathrm{I}]_t$ is the concentration of initiator consumed, and f is the initiator efficiency.

If the initiator decomposition rate constant is known, the initiator consumption can be estimated using Eqn 6:

$$[\mathrm{I}]_o - [\mathrm{I}]_t = [\mathrm{I}]_o(1 - \mathrm{e}^{-k_\mathrm{d}t}) \qquad (6)$$

The fraction of living chains (L) in RAFT polymerization (assuming no other side reactions) is given by Eqn 7:

$$L = \frac{[\mathbf{1}]_o}{[\mathbf{1}]_o + df([\mathrm{I}]_o - [\mathrm{I}]_t)} \qquad (7)$$

In Fig. 13 we show the usual plot of the dependence of molecular weight and polydispersity on conversion for a RAFT polymerization of MMA. The initiator concentration was about sixfold lower than the RAFT agent concentration. The polydispersity observed at high conversion is very low ($\overline{M}_w/\overline{M}_n < 1.1$). However, Eqn 1 significantly overestimates the molecular weight. Eqn 5 provides a prediction that is within experimental error of the experimentally determined molecular weights. In the latter calculation, we have assumed that the initiator efficiency is constant with conversion. In fact, the initiator efficiency is likely to reduce with conversion (higher viscosity), and this possibly accounts for the molecular weight at high conversion being slightly underestimated.

It is also possible to calculate the fraction of living chains based on the difference between the experimental molecular weight and that predicted by Eqn 1 by using Eqn 8. Fig. 14 shows the dependence of the fraction of living chains on RAFT agent concentration for a series of polymerizations carried out with the same reaction times and initiator levels. All polymerizations gave narrow polydispersity products ($\overline{M}_w/\overline{M}_n < 1.2$).

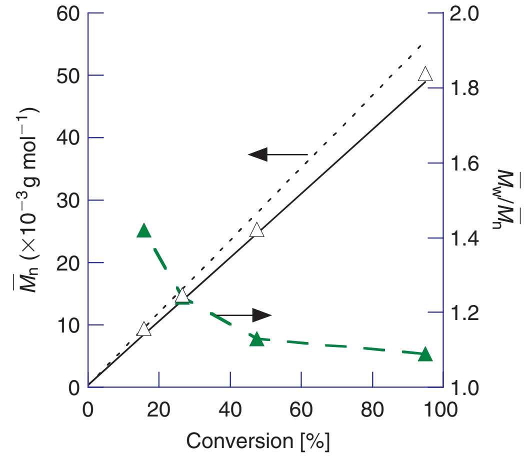


Fig. 13. Molecular weight/conversion data for the polymerization of MMA (6.55 M) in the presence of RAFT agent **64** (0.0113 M) with 1,1′-azobis(1-cyclohexanenitrile) (0.0018 M) as initiator at 90°C. The plot shows: experimental $\overline{M}_n$ (△); $\overline{M}_n$ calculated with Eqn 1 (- - - -); $\overline{M}_n$ calculated with Eqn 5 and with f 0.5, d 1.67 and k_d 2.54×10^{-5} M^{-1} s^{-1} (—); experimental $\overline{M}_w/\overline{M}_n$ (▲); line of best fit (– – – –).

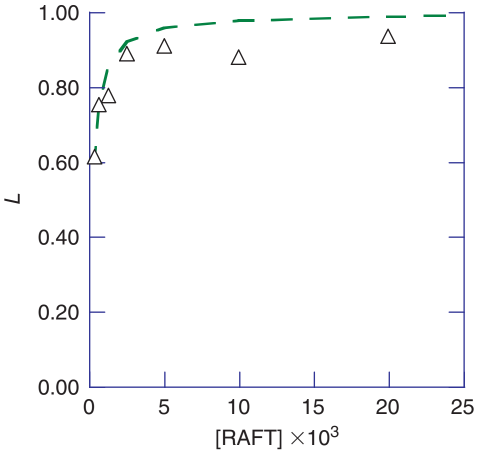


Fig. 14. Fraction of living chains (L) calculated using Eqn 8 (△) and predicted using Eqn 7 (– – – –) with cumulative f 0.3, d 1.67, and k_d 2.54×10^{-5} M^{-1} s^{-1} for PMMA formed by polymerization of MMA (6.55 M in benzene) with 1,1′-azobis(1-cyclohexanenitrile) (0.0018 M) as initiator and various concentrations of RAFT agent **64** for 6 h at 90°C (corresponds to experiments shown in Fig. 3 and Table 1).

$$L = \frac{(\overline{M}_n - m_\mathrm{RAFT})[\mathbf{1}]_o}{([\mathrm{M}]_o - [\mathrm{M}]_t) m_\mathrm{M}} \qquad (8)$$

One method for gaining further insight into the RAFT mechanism is through the use of kinetic simulation. Our first paper on kinetic simulation of the RAFT process was published in 1998.[152] Many papers have now been written on kinetic simulation of the RAFT process. Zhang and Ray,[153] and Wang and Zhu[154,155] have used a method of moments. Shipp and Matyjaszewski,[156] and Barner-Kowollik and coworkers[54,55,138,157] have used a commercial

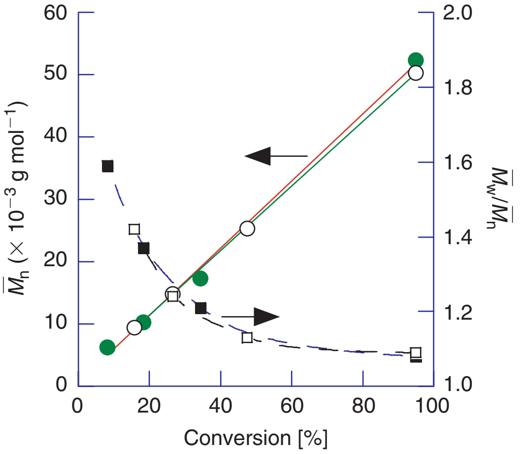


Fig. 15. Evolution of molecular weight (○,●) and polydispersity (□,■) with conversion for MMA polymerizations with RAFT agent **64** (0.0112 M) and: (*a*) MMA (7.0 M) with AIBN (0.0061 M) at 60°C (filled symbols); (*b*) MMA (6.55 M) with 1,1′-azobis(1-cyclohexanenitrile) (0.0018 M) at 90°C (open symbols).

software package (*Predici*) to evaluate complete molecular-weight distributions. Peklak et al.[158] have used a coarse-graining approach to give molecular-weight distributions. We have applied a hybrid scheme in which the differential equations are solved directly to give the complete molecular-weight distribution to a finite limit (DP < 500), and a method of moments is then used to provide closure to the equations, accurate molecular weights, and polydispersities.[44,46,152] Much of the research in this area has been carried out with a view to understanding the factors which influence retardation.[159,160] Unfortunately, many studies have made use of a simplified mechanism which in some cases may compromise the findings. The main difficulty in modelling RAFT lies in choosing values for the various rate constants.

Reaction Conditions (Temperature, Pressure, Solvent, Lewis Acids)

There have been no comprehensive studies of the effect of temperature on the course of RAFT polymerization. Temperatures reported for RAFT polymerization range from ambient to 140°C. There is evidence with dithiobenzoates that retardation is less at higher temperatures and also data that show narrower molecular-weight distributions can be achieved at higher temperatures.[7] For MMA polymerization with trithiocarbonate **64** there appears to be no dramatic effect of temperature on the molecular-weight distribution (Fig. 15). It should be noted, however, that higher temperatures offer higher rates of polymerization allowing a given conversion to be achieved in a shorter reaction time.

RAFT polymerizations under very high pressure (5 kbar) have been reported.[161–163] At high pressure, radical–radical termination is slowed and this allows the formation of higher-molecular-weight polymers and higher rates of polymerization than are achievable at ambient pressure.

The RAFT process is compatible with a wide range of reaction media including protic solvents such as alcohols and water[13,14,164,165] and less conventional solvents such as ionic liquids[166] and supercritical carbon dioxide.[167] RAFT polymerization has been successfully carried out in aqueous media. However, care should be taken because certain RAFT agents show some hydrolytic sensitivity.[243] We have found that this roughly correlates with activity of the RAFT agent (dithiobenzoates > trithiocarbonates ≈ aliphatic dithioesters).

RAFT polymerization can be conducted in the presence of Lewis acids. There are reports of attempted tacticity control of homopolymers[91,168–170] (to enable the synthesis of stereoblock copolymers[171]) and control of the alternating tendency for copolymerizations[172,173] through the use of Lewis acids as additives. For MMA polymerization, the addition of the Lewis acid scandium triflate, $Sc(OTf)_3$, increases the fraction of isotactic triads and enhances the rate of polymerization in conventional radical[174] and RAFT processes.[168,170,171] Polymerizations with dithiobenzoate RAFT agents **8**[170] or **22**[168,170,171] and $Sc(OTf)_3$ gave poor control over molecular weight and polydispersity. We[170] have shown by NMR analysis that the poor results can be attributed to the Lewis acid causing degradation of the dithiobenzoate RAFT agents; and further we have shown that trithiocarbonates are substantially more stable. Thus, polymerizations with the trithiocarbonate RAFT agent **58** provided polymer with narrow molecular-weight distributions ($\overline{M}_w/\overline{M}_n \approx 1.2$ at >95% conversion) and molecular weights as anticipated for the RAFT process, as well as the expected effect on tacticity.

RAFT in Heterogeneous Media

Much has now been written on RAFT polymerization in emulsion and mini-emulsion conditions. Our first communication on RAFT polymerization briefly mentions the successful emulsion polymerization of butyl methacrylate with cumyl dithiobenzoate as a table entry.[13] Additional examples and brief discussion of some of the important factors for successful use of RAFT polymerization in emulsion and mini-emulsion were provided in a subsequent paper.[9] Much research has shown that the success in RAFT emulsion polymerization depends strongly on the choice of RAFT agent and polymerization conditions.[9,175–183] Most work has focussed on styrene polymerization,[9,176,177,183] although RAFT emulsion polymerizations of BA[178] and methcrylates[9,13] have also been reported. Use of cumyl dithiobenzoate **22** as RAFT agent in ab initio emulsion polymerization of styrene is not recommended.[9]

The emulsion recipes we reported[9,13] were feed processes in which conversion of monomer into polymer was maintained at a high level (often >90%). In a first ab initio step, a low-molecular-weight polymeric RAFT agent was prepared. Control during this stage was not always good. However, the poorer polydispersity obtained in this step does not substantially affect control exerted during the later stages of polymerization.

A novel approach to RAFT emulsion polymerization has been reported recently.[103,181] In a first step, a water-soluble monomer (AA) was polymerized in the water phase to a low degree of polymerization to form a macro-RAFT agent.

Table 9. RAFT homo- and co-polymerization of various monomers

Monomer[A] (conc. [M])	RAFT agent (conc. [M × 10^2])	Initiator[B] (conc. [M × 10^3]) and conditions	Conversion [%]	$\overline{M}_n$[C] [g mol^{-1}]	$\overline{M}_w/\overline{M}_n$
MA (4.44)	**44** (0.37)	AIBN (0.332) 60°C, benzene, 6 h	82	96200	1.07
AA (5.83)	**8** (0.36)	AIBN (0.33) 60°C, MeOH, 16 h	53	66800[D]	1.13
S (8.7)	**8** (0.98)	110°C, 16 h	87	48000	1.07
MMA (7.48)	**22** (1.1)	Bz_2O_2 (4.0) 60°C, benzene, 16 h	78	47000	1.04
MMA (7.01)	**22** (14.7)	AIBN (30.5) 60°C, MEK, 24 h	90	6300	1.19
MMA (7.48)	**11** (1.2)	AIBN (6) 60°C, benzene, 16 h	92	55300	1.05
DMAEMA (2.54)	**12** (0.72)	ACP (1.7) 60°C, EtAc, 16 h	62	21500	1.13
DAGMA (0.77)	**8** (3.95)	V88 (2.4) 90°C, benzene, 20 h	70	3700	1.16
VAc (10.86)	**65** (9.96)	V88 (87) 100°C, 4 h	66	7000	1.18
VAc (10.86)	**50** (4.98)	AIBN (61) 60°C, 16 h	96	22700	1.24
NVP (6.0)	**65** (1.2)	AIBN (2) 60°C, MeOH, 8.5 h	53	17000	1.35
AN (6.07)	**44** (0.6)	V88 (0.33) 90°C, DMF, 16 h	30	20500[E]	1.23
NIPAM (1.77)	**22** (0.39)	AIBN (0.117) 60°C, benzene, 24 h	56	24500	1.15
Diacetone acrylamide (1.2)	**44** (2.17)	ACP (4.0) 65°C, MeOH, 4 h	89	6600	1.21
SSO_3Na (1.21)	**10** (1.66)	ACP (4.2) 70°C, H_2O, 14 h	84	10500	1.20
S-AN[C]	**22** (1.23)	100°C, 18 h	71	51400	1.07
MMA-HEMA (4.20 M/0.42)	**22** (1.11)	AIBN (6.1) 60°C, EtOAc, 16 h	75	28000	1.21
VDC-BA (6 M/1.5)	**58** (1.08)	V88 (4.0) 80°C, BuAc, 20 h	72	32800	1.38
IP-AN (5.6 M/2.4)	**58** (2.09)	V88 (4.0) 88°C, BuAc, 32 h	30	11000	1.23
S-NPMI (3.0 M/1.0)	**22** (1.04)	V88 (2.95) 90°C, toluene, 6 h	68	29600	1.11
S-NPMI (1.0 M/1.0)	**22** (10)	V88 (3.28) 90°C, toluene, 8 h	60	1600	1.10

[A] For monomer abbreviations, see footnote B of Table 2.

[B] Abbreviations: ACP, 4,4′-azobis(4-cyanopentanoic acid); AIBN, 2,2′-azobis(isobutyronitrile); V88, 1,1′-azobis(cyclohexanecarbonitrile); Bz_2O_2, dibenzoyl peroxide; BuAc, butyl acetate; EtAc, ethyl acetate; MEK, butan-2-one; MeOH, methanol.

[C] Bulk, S/AN 62 : 38 (azeotropic composition).

[D] After methylation with tetramethylammonium hydroxide/methyl iodide.

[E] Absolute molecular weight determination by light scattering.

A hydrophobic monomer (BA) was then added under controlled feed to give oligomers that form rigid micelles. These constitute a RAFT-containing seed. Continued controlled feed of hydrophobic monomer may be used to continue the emulsion polymerization. The process appears directly analogous to the 'self-stabilizing lattices' approach we have previously used in macro-monomer RAFT polymerization which involves sequential polymerization of methacrylic acid and non-polar methacrylates.[184] Both processes allow emulsion polymerization without added surfactant.

RAFT in mini-emulsion has also been reported.[9,68,82,102,185–195] We showed that RAFT in mini-emulsion can be used to produce polystyrene of narrow polydispersity in a batch process.[9] Some retardation is observed with dithiobenzoate RAFT agents.[9,82] However, this is markedly reduced when aliphatic dithioesters[82] or trithiocarbonate RAFT agents are used.[102] One of the issues with traditional mini-emulsion polymerization is the high level of surfactant and co-stabilizer that is typically employed. Pham et al.[102] have recently described surfactant-free mini-emulsion polymerization. Amphipathic macro-RAFT agents synthesized in situ by polymerization of AA were used as the sole stabilizers. This process eliminated secondary nucleation of new particles and led to a latex with no labile surfactant and good particle size control.

RAFT Polymer Syntheses

Some results for RAFT polymerizations taken from our own work are summarized in Table 9. Conversions listed are those obtained for the conditions and times stated. They are not limiting conversions or optimized reaction conditions. The data are intended to demonstrate the applicability of RAFT polymerization to a wide range of monomers under a wide range of reaction conditions. The process has been used to prepare both high- and low-molecular-weight polymers and copolymers with narrow-molecular-weight distributions. The results in Table 9 also demonstrate the compatibility of RAFT polymerization with various functional monomers.

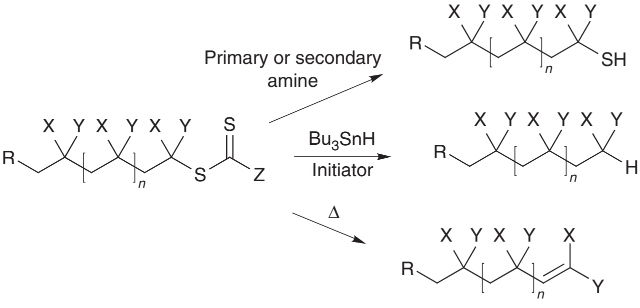
End-Functional Polymers and End-Group Transformations

One significant advantage of RAFT over other processes for living polymerization is its compatibility with protic and other functionality (e.g. OH, SO_3^-, CO_2H) present in the monomer or the RAFT agent. This makes the technique eminently suitable for the synthesis of end-functional polymers by incorporating the functionality into the Z or R groups of the RAFT agent. Functional RAFT agents include **11**, **14** (–OH); **12, 15**, **57**, **59**, **61**, **63**, **64** ($-CO_2H$); **10** ($-CO_2Na$); and **13** ($-SO_3Na$). References to the synthesis and use of these RAFT agents can be found in Tables 2 and 5. Additional examples are provided in Table 9.

The synthesis of polymers with primary or secondary amine functionality presents a problem since these amines undergo facile reaction with thiocarbonylthio compounds. Thus, amine end-functional polymers cannot be prepared directly. Such polymers can be indirectly prepared by using RAFT agents with latent amine functionality, such as the phthalimido group in RAFT agents **56** and **60**,[15] which can be subsequently deprotected.

A key feature of RAFT is that the thiocarbonylthio group(s), present in the initial RAFT agent, is(are) retained in the polymeric product(s). The retention of these groups is responsible for the polymers' living character. The products are themselves RAFT agents. However, the presence of the thiocarbonylthio groups also means that the polymers synthesized by RAFT polymerization are usually coloured. This colour may range from violet through red to pale yellow depending on the absorption spectrum of the particular thiocarbonylthio chromophore. The presence of colour can be disadvantageous in some applications. Even though colour may be modified by appropriate selection of the initial RAFT agent, there has nonetheless been some incentive to develop effective methods for treatment of RAFT-made polymer to cleave the thiocarbonylthio end groups post polymerization.

In some circumstances, it is also necessary or desirable to deactivate thiocarbonylthio groups because of their reactivity or to transform them for use in subsequent processing. For certain applications, it is desirable to have polymers possessing thiol functionality. These applications include the use of bisthiols in the synthesis of condensation polymers such as polythiourethanes or polythioesters. Thiol functionality may also be used to form crosslinks. Other applications of thiol functional polymers relate to the property of thiols to complex metals and to form conjugates with biological polymers, such as proteins.[95,196]



Scheme 15.

Some of the processes that have been used for thiocarbonylthio group removal/transformation are shown in Scheme 15. They include hydrolysis/aminolysis, various radical induced reactions, and thermal elimination.[15,101] The RAFT end-group is also light sensitive and can be removed under UV irradiation;[70] it may be oxidized with reagents such as peroxides or sodium hypochlorite.[13]

The kinetics and mechanism of the reaction of compounds containing thiocarbonyl groups with nucleophiles has been reviewed by Castro.[197] It is well known that thiocarbonylthio groups can be transformed into thiols by reaction with nucleophiles which include pyridines, primary and secondary amines, ammonia, other thiols, and hydroxide. They may also be reduced to thiols with hydride reducing agents such as sodium borohydride, lithium aluminum hydride, or with zinc in acetic acid. The thiocarbonylthio groups in RAFT-synthesized polymers are subject to the same reactions. The potential of this chemistry to cleave end groups and decolourize polymers and produce polymers with thiol end groups was cited in our initial communication on RAFT polymerization.[13] Examples of end-group cleavage with nucleophiles such as amines,[15,96,198,199] hydroxide,[93] and borohydride[164,200] can be found in recent publications. Radical induced reduction with, for example, tri-*n*-butylstannane[15,201,202] can be used to replace the thiocarbonylthio group with hydrogen.

RAFT end groups are known to be unstable at very high temperatures. At temperatures >200°C, thermal elimination has been used as a means of trithiocarbonate end-group removal from polystyrene or poly(butyl acrylate).[15,101] Thermal C—S bond homolysis is also possible. Depending on the propagating chain and the RAFT group, these reactions may also occur at lower temperatures and will set an upper temperature limit for the RAFT process.

Gradient Copolymers

In most copolymerizations, the monomers are consumed at different rates dictated by the steric and electronic properties of the reactants. Consequently, both the monomer feed and copolymer composition will drift with conversion. Thus conventional copolymers are generally not homogeneous in composition at the molecular level. In RAFT polymerization processes, where all chains grow throughout the polymerization, the composition drift is captured within the chain

Table 10. Preparation of gradient copolymers by copolymerization of methyl acrylate (MA) and vinyl acetate (VAc) in the presence of *O*-ethyl *S*-cyanomethyl xanthate 65[A]

Time [h]	Conversion [%]	$\overline{M}_n$[B]	$\overline{M}_w/\overline{M}_n$	Cumulative MA [%][C]	Interval MA [%][D]
2	32	7700	1.57	77	77
4	50	9400	1.54	69	55
8	59	9800	1.41	60	0
16	70	14000	1.34	49	0

[A] Bulk MA/VAc (34 : 66 mol ratio) with AIBN (0.0031 M) and **65** (0.025 M) at 60°C.
[B] Molecular weight in polystyrene equivalents.
[C] Cumulative percentage of MA in copolymer determined by ^{1}H NMR spectroscopy.
[D] Composition of copolymer formed in the interval between the shown time point and the immediately preceeding time point.

Table 11. Preparation of gradient copolymers by copolymerization of styrene (S) and *N*-phenylmaleimide (NPMI) in the presence of cumyl dithiobenzoate 22[A]

Time [h]	Conversion [%]	$\overline{M}_n$[B]	$\overline{M}_w/\overline{M}_n$	Cumulative NPMI/S[C]	Interval NPMI/S[D]
0.5	31	13900	1.12	50 : 50	50 : 50
1	46	20500	1.10	50 : 50	50 : 50
3	62	27200	1.10	44 : 56	29 : 71
6	68	29600	1.11	40 : 60	0 : 100
16	74	33300	1.13	36 : 64	0 : 100

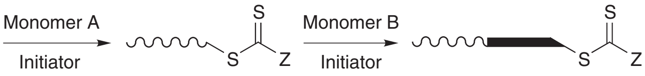
[A] S (3.0 M) and NMPI (1.0 M) in toluene with 1,1′-azobis (1-cyclohexanenitrile) (0.00295 M) and **22** (0.0104 M) at 90°C.
[B] Molecular weight in polystyrene equivalents.
[C] Cumulative NPMI/S in copolymer determined by ^{1}H NMR spectroscopy.
[D] Composition of copolymer formed in the interval between the shown time point and the immediately preceeding time point.

structure. All chains have similar composition and are called gradient or tapered copolymers.

Copolymers (e.g. S—AN, MMA—HEMA, see Table 9) when formed in the presence of a RAFT agent have the same overall composition and sequence distribution (NMR) as those formed in the absence of a RAFT agent. Reactivity ratios are unaffected by the RAFT process. However, for very low conversions when molecular weights are low, copolymer composition may be different for that seen in conventional copolymerization because of specificity shown by the initiating species (R).[203]

A difference between copolymers synthesized by RAFT copolymerization and those synthesized by conventional radical copolymerization is that copolymers formed by RAFT copolymerization are gradient copolymers whereas those formed by the conventional process are blends. It is possible to synthesize block polymers in a batch polymerization by taking advantage of disparate reactivity ratios between particular monomer pairs (BA-MMA,[5,7] tBA-VAc,[110] S-MAH[51,70,79,80]). The composition can be further tailored by use of suitable monomer feed protocols. In general, it is important in designing copolymerizations to choose a RAFT agent that is compatible with all the monomers in the feed. RAFT copolymerization can be successful (provide molecular weight control and narrow molecular weight distributions) even when one of the monomers is not amenable to direct homopolymerization using a particular RAFT agent. RAFT polymerization of MMA with benzyl dithiobenzoate provides very poor control yet copolymerization of S with MMA succeeds while the medium contains some (approx. 5%) styrene.

An example of gradient copolymer formation is the batch copolymerization of MA and VAc. The reactivity ratios ($r_{\mathrm{MA}} \approx 9$, $r_{\mathrm{VAc}} \approx 0.1$) are such that both propagating radicals prefer to add to MA. Thus, MA-VAc copolymerization in the presence of a xanthate RAFT agent provides copolymer chains that are rich in MA at one end and rich in VAc at the other. The results of one such experiment are shown in Table 10. When a mixture of MA and VAc (34 mol % M) was copolymerized with AIBN in the presence of *O*-ethyl *S*-cyanomethyl xanthate **65** at 60°C, the first-formed polymer (at 2 h) is predominantly composed of MA units, and the product following exhaustion of this monomer is poly(methyl acrylate-*co*-vinyl acetate)-*block*-poly(vinyl acetate).



Scheme 16. A–B diblock synthesis.

Another example is the copolymerization of styrene (S) with *N*-phenylmaleimide (NPMI; Table 11). In this case, the reactivity ratios ($r_{\mathrm{S}} \approx 0.02$, $r_{\mathrm{NPMI}} \approx 0.04$) are such that the two monomers have a strong tendency to alternate in the chain. When the copolymerization is conducted with an excess of styrene the product is poly(*N*-phenylmaleimide-*alt*-styrene)-*block*-polystyrene. It is thus possible to use RAFT polymerization to prepare block copolymers in a 'one-pot' batch polymerization process.

Diblock Copolymers

RAFT polymerization is recognized as one of the most versatile methods for block copolymer synthesis and numerous examples of block synthesis have now appeared in the literature. RAFT polymerization proceeds with retention of the thiocarbonylthio group. This allows an easy entry to the synthesis of AB diblock copolymers by the simple addition of a second monomer (Scheme 16).[77] Higher order (ABA, ABC, etc.) blocks are also possible by sequential addition of further monomer(s). The results of several such experiments are summarized in Table 12. References to other diblock syntheses are provided in Tables 2–6.

Of considerable interest is the ability to make hydrophilic–hydrophobic block copolymers where the hydrophilic block is composed of unprotected polar monomers such as acrylic acid, dimethylaminoethyl methacrylate, or ethylene oxide. A doubly hydrophilic block composed of acrylic acid and *N*-isopropylacrylamide (NIPAM) segments has also been prepared.[95] Other examples of doubly hydrophilic block copolymers have been reported by McCormick and coworkers.[244–247]

In RAFT polymerization, the order of constructing the blocks of a block copolymer can be very important.[44,77] The

Table 12. A–B diblock copolymers by RAFT polymerization[A]

RAFT agent	A-Block	$\overline{M}_n$	A–B Diblock	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Refs
22	MMA	55000	MMA-*b*-S	112500	1.20	
22	MMA	3200	MMA-*b*-MAA	4700	1.18	[38,77]
22	BzMA	1800	BzMA-*b*-DMAEMA	3500	1.06	[38,77]
22	tBA	2100	AA-*b*-NIPAM[D]	5400[E]	1.10[E]	
21	BA	33600	BA-*b*-AA	52400	1.19	[38,77]
20	S	20300	S-*b*-DMA	43000	1.24	[38,77]
12	DMAEMA	63600[B]	DMAEMA-*b*-S	103900[B]	1.28	
12	EO	750	EO-*b*-S[C]	7800	1.07	[38,77]

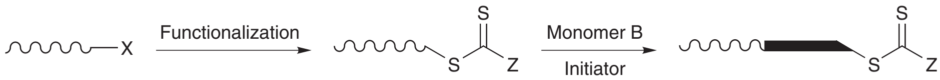
[A] For abbreviations see footnote A to Table 2.

[B] GPC with DMF as eluent.

[C] Prepared from dithioester terminated poly(ethylene oxide).

[D] AA-*b*-NIPAM obtained after hydrolysis of the tBA-*b*-NIPAM with formic acid.

[E] Calculated from the GPC determined $\overline{M}_n$ of tBA-*b*-NIPAM.



Scheme 17. A–B diblock synthesis from end-functional polymers via the RAFT process.

propagating radical for the first formed block must be a good homolytic leaving group with respect to that of the second block. For example, in the synthesis of a methacrylate–acrylate or methacrylate–styrene diblock, the methacrylate block should be prepared first.[53,77] The styrene or acrylate propagating radicals are very poor leaving groups with respect to methacrylate propagating radicals.

Block copolymers based on polymers formed by other mechanisms can be prepared by forming a pre-polymer containing thiocarbonylthio groups and using this as a macro-RAFT agent (Scheme 17).[77,110] We first exploited this methodology to prepare poly(ethylene oxide)-*block*-PS from commercially available hydroxy end-functional poly(ethylene oxide) (last example in Table 12).[77,110] Other block copolymers that have been prepared using similar strategies include poly(ethylene-*co*-butylene)-*block*-poly(S-*co*-maleic anhydride),[70] poly(ethylene oxide)-*block*-poly(MMA),[204] poly(ethylene oxide)-*block*-poly(N-vinylformamide),[205] poly(ethylene oxide)-*block*-poly(NIPAM),[206] poly(ethylene oxide)-*block*-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate),[207] poly(lactic acid)-*block*-poly(MMA),[204] and poly(lactic acid)-*block*-poly(NIPAM).[208,209]

Triblock Copolymers

A–B–A triblock copolymers can be prepared by RAFT polymerization in several different ways. One is to chain extend an A–B diblock with monomer A. However, the use of a bis-RAFT agent as a triblock precursor means that triblock synthesis can be accomplished in only two polymerization steps and helps ensure that both arms are of the same length and composition.[14,77,96]

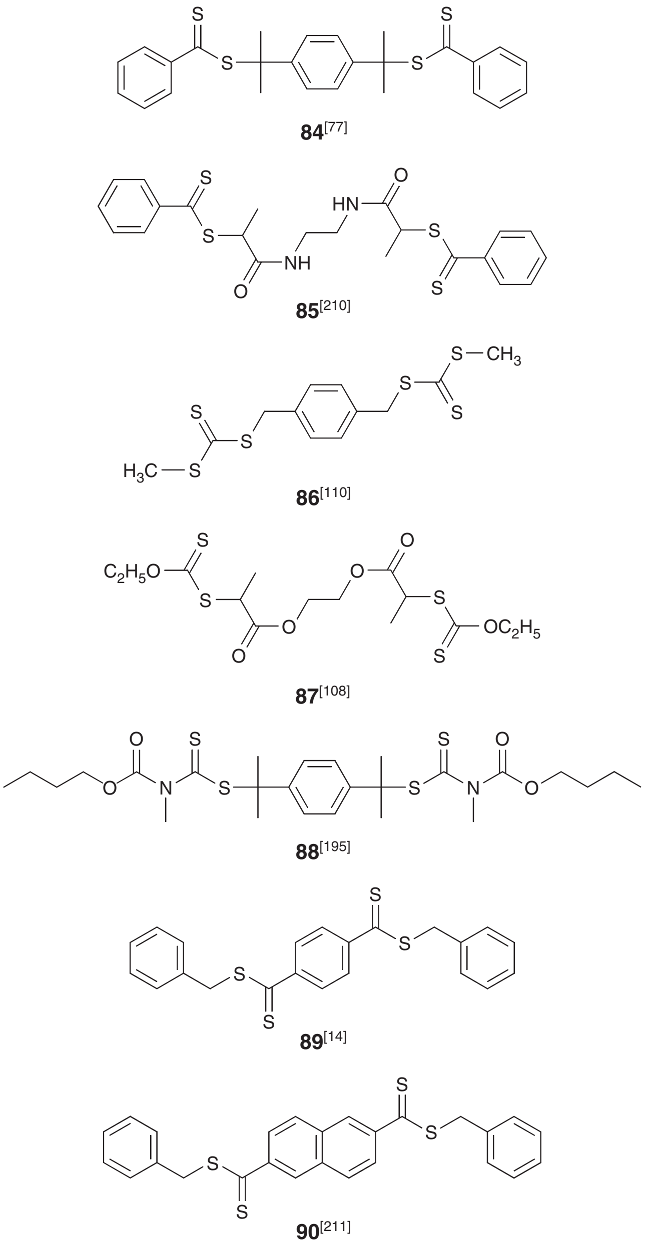
There are two main classes of bis-RAFT agent. With the bis-dithioesters **84**[77] or **85**,[210] the bis-trithiocarbonate **86**,[110] the bis-xanthate **87**,[108] or bis-dithiocarbamate **88**[195] the polymer is grown out from the core and the RAFT functionality is retained at the chain ends. With symmetrical trithiocarbonates (e.g. **54**–**57**)[96,99] or bis-RAFT agents such as **89**[14] or **90**,[211] the RAFT functionality remains in the centre of the block (Scheme 18). The merits and demerits of the two approaches will be discussed further in the section on star polymers.

Some recent work has been orientated towards the synthesis of triblocks intended as thermoplastic elastomers based on a 'soft' acrylate mid-section and 'hard' styrene or styrene-*co*-acrylonitrile outer blocks (Scheme 19).[110] Rather than have labile functionality internal to the triblock, the RAFT agent **86** was chosen so that the thiocarbonylthio functions would remain at the chain ends (methyl is a very poor free-radical leaving group). The α,ω-bis(methylsulfanylthiocarbonylsulfanyl)–poly(butyl acrylate), $\overline{M}_n$ 77000, $\overline{M}_w/\overline{M}_n$ 1.05, was formed by solution polymerization at 60°C with AIBN initiator, and this was converted into a triblock copolymer $\overline{M}_n$ 171000, $\overline{M}_w/\overline{M}_n$ 1.12 by heating styrene/acrylonitrile (62 : 38 mol ratio, azeotropic composition) at 110°C in a subsequent step (Fig. 16). A series of such block copolymers of varying block length and composition was made to enable a structure property correlation to be established. It was found that narrow polydispersities for both the mid- and end-blocks were critical to achieving optimal mechanical properties.

Star Polymers

There are now a large number of papers on the synthesis of star polymers using the RAFT process. The most common approach begins with a compound containing multiple thiocarbonylthio groups of appropriate design; a multi-RAFT agent. The synthesis of star polymers from multi-RAFT agents can be seen as an extension of the triblock syntheses described above where the number of thiocarbonylthio groups exceeds two. The multi-RAFT agent may be a small organic compound,[6,9,77,110,198,212–214] an organometallic complex,[215] a dendrimer,[216–218] a hyperbranched species,[219] a macromolecular species,[204,220] a particle, or indeed, any moiety possessing multiple thiocarbonylthio groups (though here the distinction between star and graft copolymers becomes blurred). Our first RAFT patent[14] recognized two limiting forms of star growth depending on the orientation of the thiocarbonylthio group with respect to the core. We have discussed the advantages and disadvantages of the 'propagation away from core' (Scheme 20) and 'propagation attached to core' (Scheme 21) strategies in various publications.[6,9,110,198]

Multi-RAFT agents are readily synthesized from the corresponding multi-thiol, multi-hydroxy, and multi-halo compounds. The challenge in preparing such multifunctional molecules lies with developing reactions that proceed in quantitative yield and produce no by-products. Whereas incomplete reaction or side reactions in the synthesis of a monofunctional compound will give residual starting materials or an easily removed by-product, in the case of multifunctional compounds such process lead to molecules with incomplete functionality. For example, in the case of an eight-armed core, a yield of 95% for an individual functionalization step means that <70% of the product would contain the requisite number of arms. Purification of mixtures of cores with different levels of functionality can be extremely difficult and the process then becomes unviable. We have reported[114] methods to quantitatively (>95% overall yield)



84[77]

85[210]

86[110]

87[108]

88[195]

89[14]

90[211]

Scheme 18.

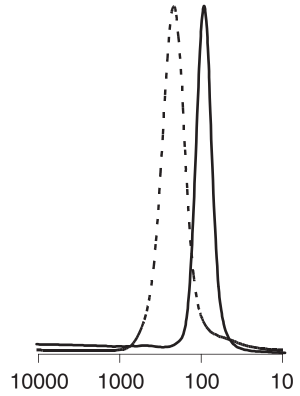
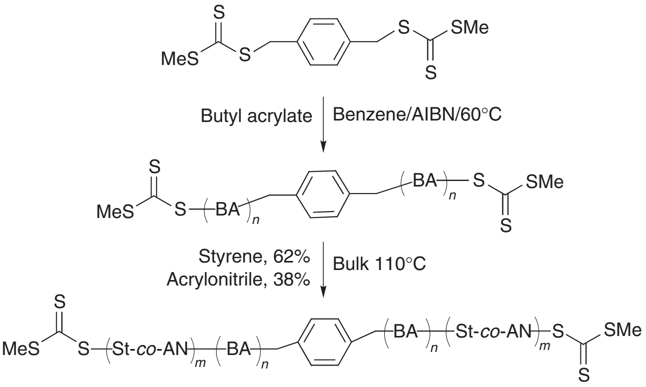
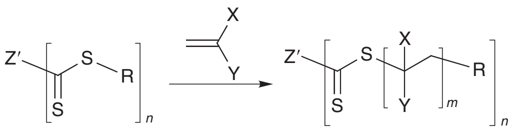


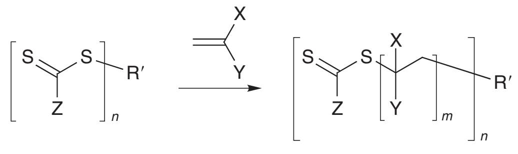
Fig. 16. Molecular-weight distributions for poly(butyl acrylate) (—) and derived triblock copolymer (- - -).



Scheme 19.



Scheme 20. Star polymer synthesis by the 'propagation away from core' strategy.



Scheme 21. Star polymer synthesis by the 'propagation attached to core' strategy.

convert multi-hydroxy compounds into both classes of multi-RAFT agent (Schemes 22 and 23), and have applied these in making three-, four-, six-, and eight-armed stars with narrow polydispersity based on trimethylolethane, pentaerythritol, dipentaerythritol, and tripentaerythritol cores respectively.

The 'propagation away from core' strategy (Scheme 20) is illustrated by the synthesis of a four-arm star from the tetra-trithiocarbonate **91** (Scheme 24, Fig. 17).[198] RAFT agents **93–95** also belong to this class (Scheme 25). The advantage of this strategy is that, since propagating radicals are never directly attached to the core, by-products from star–star coupling are unlikely (Scheme 26). Radical–radical termination will involve linear propagating radicals **97** and will produce a low-molecular-weight by-product that may be observed in high conversion polymerizations (for example, Fig. 17). All of the thiocarbonylthio functionality remains at the core of the star structure. It might be envisaged that steric factors

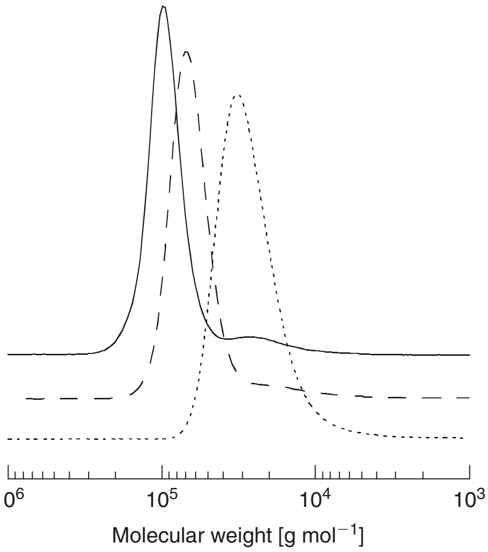


Fig. 17. Molecular-weight distributions obtained during bulk thermal polymerization of styrene at 110°C with tetrafunctional RAFT agent **91** (0.0074 M). From bottom to top: at 6 h, 25% conversion, $\overline{M}_n$ 25550, $\overline{M}_w/\overline{M}_n$ 1.2; at 20 h, 63% conversion, $\overline{M}_n$ 63850, $\overline{M}_w/\overline{M}_n$ 1.1; at 64 h, 96% conversion, $\overline{M}_n$ 92100, $\overline{M}_w/\overline{M}_n$ 1.2. The small peak to lower molecular weight seen at high conversion can be attributed to dead linear chains. This peak is not observed by GPC with UV detection.

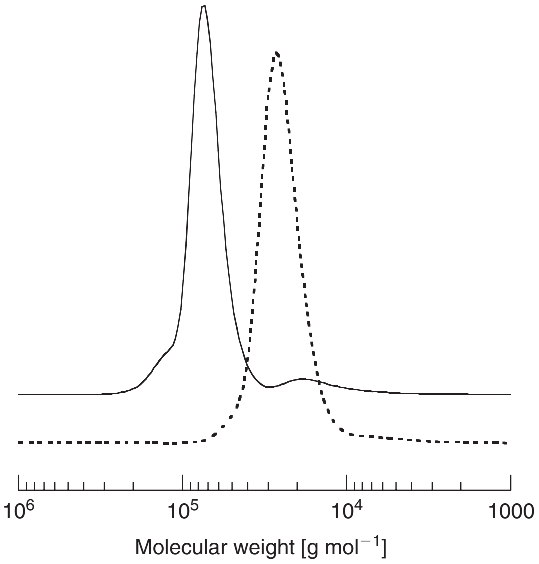
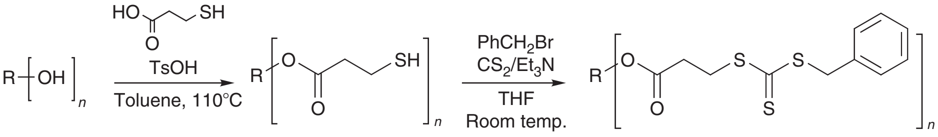
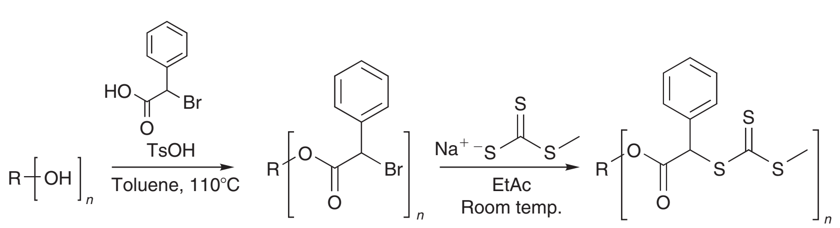


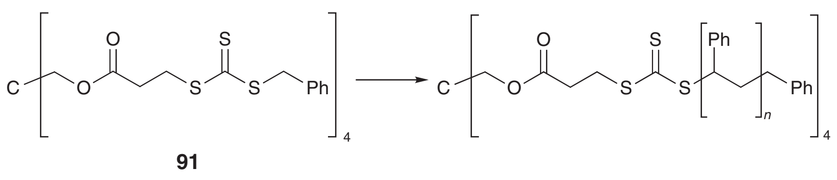
Fig. 18. Molecular weight distributions obtained during bulk thermal polymerization of styrene at 110°C with tetrafunctional RAFT agent **92** (0.0074 M). From bottom to top: at 6 h, 24% conversion, $\overline{M}_n$ 24300, $\overline{M}_w/\overline{M}_n$ 1.1; at 48 h, 96% conversion, $\overline{M}_n$ 70700, $\overline{M}_w/\overline{M}_n$ 1.2. The small peak to lower molecular weight seen at high conversion can be attributed to linear dormant chains. The high-molecular-weight shoulder can be attributed to star–star coupling. These peaks are also observed by GPC with UV detection.



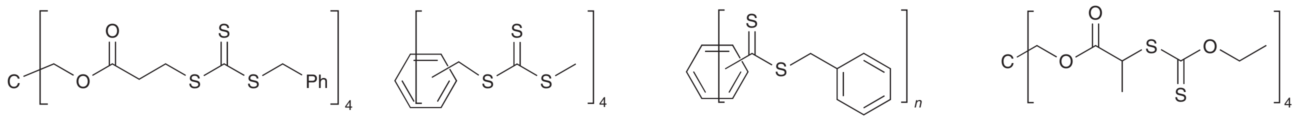
Scheme 22.



Scheme 23.



Scheme 24.



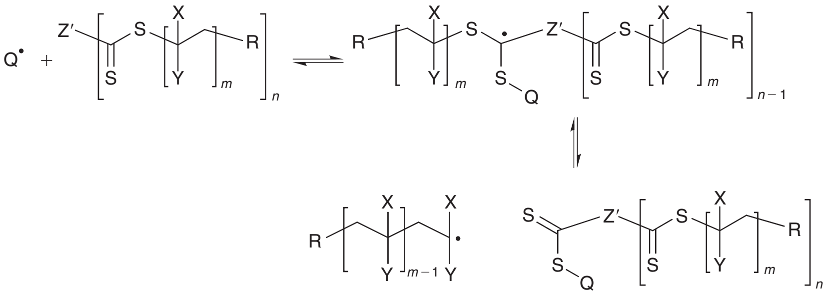
91[198]

92[198]

93 $n = 3$ (1,3,5-substitution)[211]
94 $n = 4$ (1,2,4,5-substitution)[77]
95 $n = 6$[77,213]

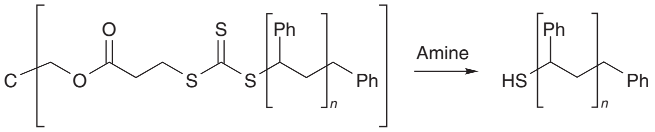
96[214]

Scheme 25.

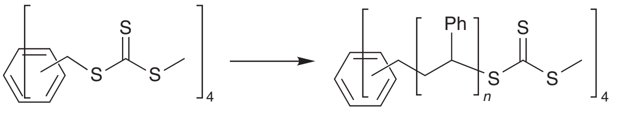


97

Scheme 26. Q• is **97** or an initiator-derived propagating radical.



Scheme 27.



92

Scheme 28.

associated with attack of the propagating radical at the core of the star would be an issue particularly at high conversions. There is, however, no direct evidence of problems attributable to this cause in the examples we have reported.

A potential disadvantage of the 'propagation away from core' strategy is that any reaction which cleaves the thiocarbonylthio groups (e.g. hydrolysis, thermolysis) results in destruction of the star structure. However, this property may be turned into an advantage in some circumstances; for example, in polymer-supported polymer synthesis. Arm cleavage also enables the molecular weights of the arms and the uniformity of arm growth to be readily verified (Scheme 27).[198]

The 'propagation attached to core' strategy (Scheme 21) is illustrated by the synthesis of a four-arm star from the tetra-trithiocarbonate **92** (Scheme 28, Fig. 18).[198] RAFT agent **96** also belongs to this class.

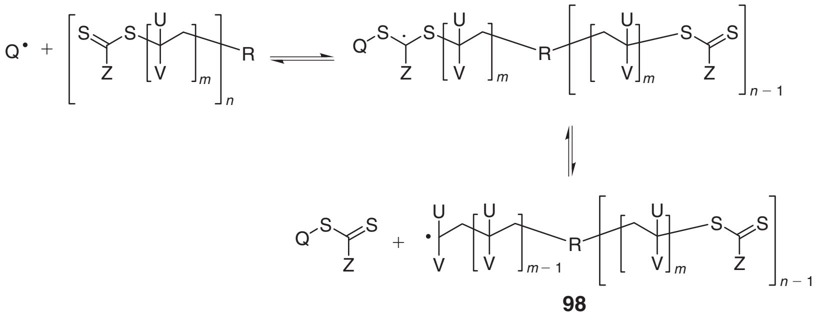
For these RAFT agents, the thiocarbonylthio functionality remains at the periphery of the star and the majority of propagating radicals will be attached to the core. Star–star coupling by self reaction of radicals **98** is therefore a potential complication (Scheme 29). A fraction of linear dormant chain commensurate with the number of initiator-derived chains will be formed as a by-product (for example, Fig. 18). The likelihood of star–star coupling is expected to increase with the number of arms to the star but can be minimized by controlling the conversion and rate of initiation.

The synthesis of stars is readily extended to star-blocks using strategies similar to those described under diblocks.[198]

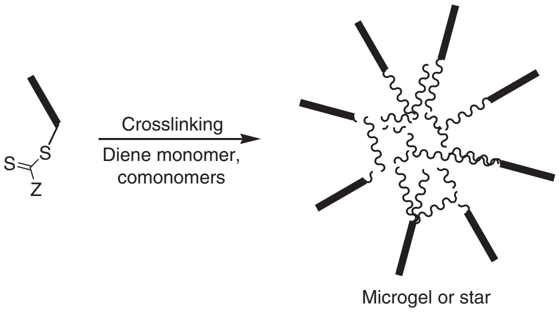
Microgels

The so called 'arm-first' process[221,222] involves making a living polymer then using this to initiate (co)polymerization of a di- (or higher) functional monomer which forms a crosslinked core (Scheme 30). The methodology has been used to make star-shaped molecules using NMP or ATRP. Again, RAFT polymerization offers new scope to this process.[223] The RAFT process usually involves (co)polymerization of an appropriate diene monomer (e.g. divinylbenzene) in the presence of a polymer formed by RAFT polymerization. Lord et al.[224] have also used this strategy to prepare star microgels.

Suitably constructed hydrophilic–hydrophobic (or solvophilic–solvophobic) block copolymers possess the ability to self-assemble to form micelles (or other supramolecular structures). Such supramolecular assemblies may only be stable in a particular medium and/or over a specific concentration range. Various crosslinking mechanisms can be used to stitch these structures together to form a stable star polymer or microgel (or other structure). The core, the shell, or mid-block section of the micelle may be crosslinked to stabilize the structure.[110,225,226] Star microgel synthesis would usually require crosslinking of the micelle's core (Scheme 31). Care is needed in selecting reaction conditions so as to



Scheme 29. Q• may be **98** or an initiator-derived propagating radical.



Scheme 30.

avoid inter-micelle crosslinking, and gel formation. Variants of this methodology have been used to prepare a range of structures.[208,227]

Polymer Brushes/Graft Copolymers

The preparation of polymer brushes by controlled radical polymerization from appropriately functionalized polymer chains, surfaces, or particles by a grafting-from approach has recently attracted a lot of attention.[228] Most work has used ATRP or NMP, though papers on the use of RAFT polymerization have begun to appear.[229–235] The first to apply RAFT in this context were Tsujii et al.[229] and Brittain and coworkers.[230,231] Recent papers describe RAFT polymerization from plasma-treated Teflon surfaces[232] and ozonolyzed polyimide films.[235] The approach used in these and most other studies[230–235] has been to immobilize initiator functionality on the surface by chemical or plasma modification and use this to initiate polymerization in the presence of a dithioester RAFT agent. Tsujii et al.[229] have indicated that some difficulties arise in using RAFT for grafting from particles because of an abnormally high rate of radical–radical termination caused by a locally high concentration of RAFT functionality.

Skaff and Emrick[236] bound RAFT agent **99** (Scheme 32) to cadmium selenide nanoparticles by a ligand-exchange process, and grew various narrow molecular-weight distribution polymers (PS, PMA, PBA, PS-MA, PS-AA, PS-IP, PS-*b*-MA, PS-*b*-BA) from these particles. Perrier and coworkers[204,237] have attached RAFT moieties to cellulose (cotton) in order to from PS, PMA, or PMMA grafts. This involved derivatization of the cellulosic OH groups with thiocarbonylthio functionality.

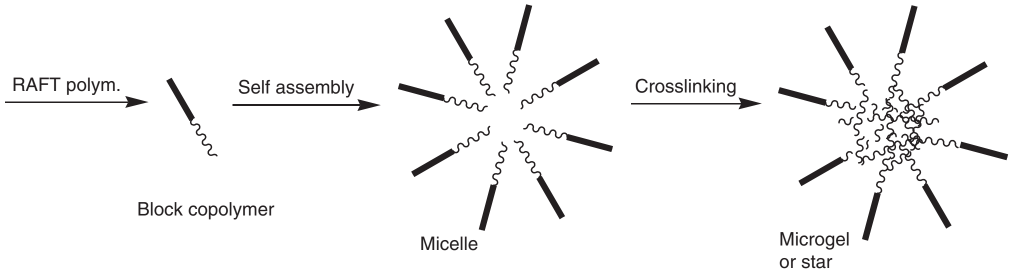
Grafting-through approaches have also been applied. There have been several studies on the graft polymers by macromonomer (co)polymerization.[238–240] End-functional polymers prepared by RAFT polymerization can be used in 'grafting-to' reactions. The property of thiols and dithioesters to bind to heavy metals such as gold and cadmium has been used in preparing brushes based on gold film or nanoparticles[200,241,248] and cadmium selenide nanoparticles.[242] RAFT-synthesized thiols have also been used to make protein conjugates.[95,196]

Summary

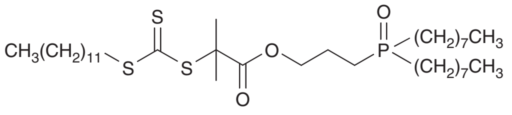
RAFT polymerization has emerged as one of the most important methods for living radical polymerization. The method is robust and versatile and can be applied to the majority of polymers prepared by radical polymerization. However, selection of the RAFT agent for the monomers and reaction conditions is crucial for success. Guidelines for selection exist and most monomers can be polymerized with good control by using one of two RAFT agents. One suited to (meth)acrylate, (meth)acrylamide, and styrenic monomers, for example, a tertiary cyanoalkyl trithiocarbonate, and another suited to vinyl monomers such as VAc, for example, a cyanoalkyl xanthate. Monomers that remain difficult to homopolymerize by the RAFT process are the olefins (ethylene, propylene). Notwithstanding these comments, many features of the kinetics of RAFT polymerization with specific RAFT agents remain to be detailed and unravelled.

RAFT polymerization can provide control over the manner of chain initiation and termination in radical polymerization. A remaining challenge in free-radical polymerization is to obtain simultaneous control over the propagation step to achieve greater chemo-, regio-, and stereo-specificity. In RAFT polymerization, all data point to the propagating radicals behaving as conventional propagating radicals. With judicious choice of RAFT agent, the reagents (e.g. Lewis acids) used to control propagation in conventional polymerization can be applied to achieve similar control during the RAFT process.

We have illustrated how the RAFT process is being used in the synthesis of well defined homo-, gradient, diblock, triblock, and star polymers as well as more complex architectures including microgels and polymer brushes. New materials that have the potential of revolutionizing a large



Scheme 31.



99

Scheme 32.

part of the polymer industry are beginning to appear. Possible applications range from novel surfactants, dispersants, coatings, and adhesives, to biomaterials, membranes, drug delivery media, and materials for microelectronics.

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Living Radical Polymerization by the RAFT Process—A First Update

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This paper provides a first update to the review of living radical polymerization achieved with thiocarbonylthio compounds (ZC(=S)SR) by a mechanism of Reversible Addition–Fragmentation chain Transfer (RAFT) published in June 2005. The time since that publication has witnessed an increased rate of publication on the topic with the appearance of well over 200 papers covering various aspects of RAFT polymerization ranging over reagent synthesis and properties, kinetics, and mechanism of polymerization, novel polymer syntheses, and diverse applications.

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Introduction

Radical polymerization is one of the most widely used processes for the commercial production of high molecular weight polymers.[1] The emergence over the last ten years of techniques for implementing living radical polymerization has provided a new set of tools for polymer chemists that allow very precise control over the polymerization process while retaining much of the versatility of conventional radical polymerization. It is no longer a formidable task to apply radical polymerization to the synthesis of blocks, stars, or other polymers of complex architecture. New materials that have the potential of revolutionizing a large part of the polymer industry continue to appear. The living radical polymerization techniques that are receiving greatest attention are nitroxide-mediated polymerization (NMP), atom-transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT). The increasing importance of RAFT in this context is illustrated by Fig. 1 that shows the increasing rate of citation of our first communication on RAFT with thiocarbonylthio compounds[2] and the first RAFT patent.[3] It should be noted that not all papers on RAFT polymerization cite these sources nor are all of the papers citing these documents relevant to RAFT polymerization.

This review is primarily intended to cover the literature on RAFT polymerization that has appeared since publication of our review of the field published in the *Australian Journal of Chemistry* in June 2005[4] and a review of similar scope contained within *The Chemistry of Radical Polymerization*.[1] We also refer to some earlier papers that were not included

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Ezio Rizzardo is a graduate of the University of New South Wales and received his Ph.D. from the University of Sydney for his studies on the photochemistry of nitro compounds. He joined CSIRO in 1976 after a postdoc at Rice University, RIMAC, and the Australian National University. His CSIRO research has focussed on developing methods for controlling free radical polymerization. For this he has received a number of awards including the RACI Australian Polymer Medal and the CSIRO Chairman's Gold Medal. Currently he is a CSIRO Fellow and a Fellow of the Australian Academy of Science.

San H. Thang was born in Saigon, Vietnam, in 1954 and came to Australia in 1979 as a refugee. He completed his B.Sc.(Hons) degree in 1983 and Ph.D. in 1987 from Griffith University. He joined CSIRO in 1986 as a research fellow. He then moved to ICI Australia in late 1987 to undertake the challenge of industrial research. He returned to CSIRO in late 1990, and in 1995 he was co-inventor of the RAFT Process. He is currently a senior principal research scientist at CSIRO Molecular and Health Technologies where his research focusses on the interface between organic and polymer chemistry.

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in that review. However, work mentioned in the previous review[4] is only mentioned again where necessary to put the more recent work in context. The last year has seen the publication of three further major reviews detailing the RAFT process.[5–7] Quiclet-Sire and Zard[8] have reviewed the application of radical addition–fragmentation processes in synthetic chemistry. Other reviews cover specific aspects of RAFT polymerization, such as computational studies related to RAFT agents and RAFT polymerization,[9] use of RAFT polymerization in heterogeneous media,[10,11] the synthesis of end functional polymers by RAFT polymerization,[12,13] the synthesis and properties of stimuli responsive block copolymers,[13] the preparation of honeycomb polymers,[14] and the control of molecular weight distributions produced by RAFT polymerization.[15] RAFT polymerization is also reviewed within works which deal more generically with radical polymerization. The process is reviewed within the chapter *Living Radical Polymerization* in *The Chemistry of Radical Polymerization*[1] and is covered in most recent reviews that, in part, relate to polymer synthesis, living polymerization, or novel architectures.[16–23] Mention should be made of the recent *ACS Symposium Series* volume *Controlled/Living Radical Polymerization: From Synthesis to Materials* in which approximately one third of the papers relate directly to RAFT polymerization.[24]

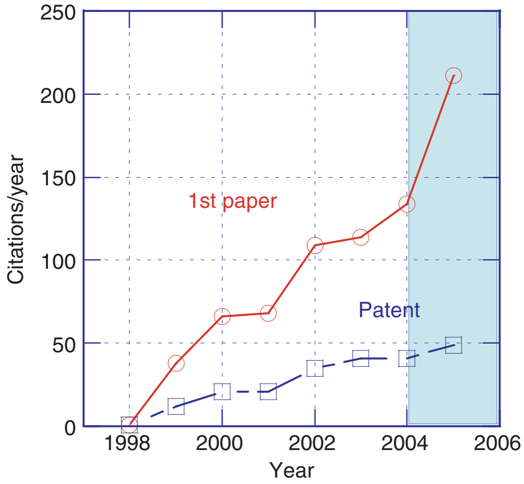
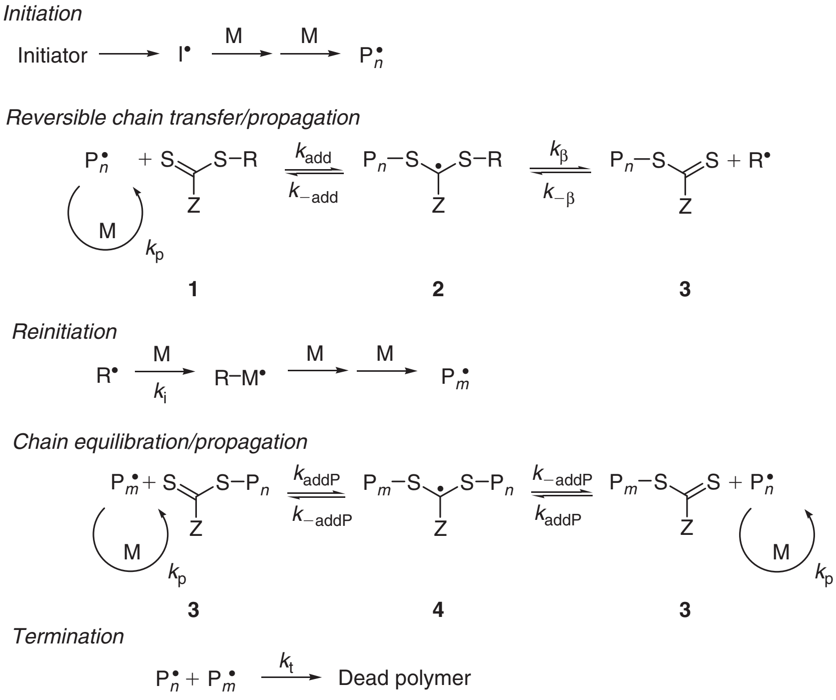


Fig. 1. Citation rate of our first communication[2] and first patent[3] on RAFT polymerization. Based on SciFinder search carried out in May 2006.

Mechanism of RAFT

The key feature of the mechanism of RAFT polymerization with thiocarbonylthio compounds as proposed in our first communication on the subject[2] is the sequence of addition–fragmentation equilibria shown in Scheme 1. Initiation and radical–radical termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical ($P_n^\bullet$) to the thiocarbonylthio compound (RSC(Z)=S, **1**) followed by fragmentation of the intermediate radical provides a polymeric thiocarbonylthio compound ($P_nS(Z)C{=}S$, **3**) and a new radical ($R^\bullet$). Reaction of this radical ($R^\bullet$) with monomer forms a new propagating radical ($P_m^\bullet$). Rapid equilibrium between the active propagating radicals ($P_n^\bullet$ and $P_m^\bullet$) and the dormant polymeric thiocarbonylthio compounds **3** provides equal probability for all chains to grow and allows for the production of narrow polydispersity polymers. When the polymerization is complete (or stopped), most chains retain the thiocarbonylthio end group and can be isolated as stable materials.



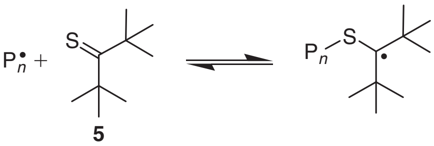
Scheme 1. Mechanism of RAFT polymerization.

The reactions associated with RAFT equilibria shown in Scheme 1 are in addition to those (i.e. initiation, propagation, and termination) that occur during conventional radical polymerization. In an ideal RAFT process, the RAFT agent should behave as an ideal transfer agent. Thus, as with radical polymerization with conventional chain transfer, the kinetics of polymerization should not be directly affected beyond those affects attributable to the differing molecular weights of the reacting species. Radical–radical termination is not directly suppressed by the RAFT process. Living characteristics are imparted when the molecular weight of the polymer formed is substantially lower than that which might be formed in the absence of a RAFT agent and the number of polymer molecules with RAFT agent derived ends far exceeds the number formed as a consequence of termination.

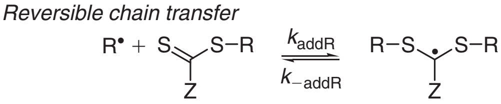
This said, RAFT polymerizations are frequently observed to stray from this ideal situation. Although the basic mechanism shown in Scheme 1 is generally not disputed, much debate continues on the kinetics of the RAFT process, the rapidity with which the various equilibria are established, and what side reactions might occur to complicate the process, the kinetics, and polymer syntheses. An IUPAC task group *Towards a Holistic Mechanistic Model for RAFT Polymerizations: Dithiobenzoates as Mediating Agents* was formed in 2005 under the auspices of the IUPAC Subcommittee on *Modeling of Polymerization Kinetics and Processes*. The first output of that working party, being a *dilemma paper* that summarizes the current situation, has just been published.[25]

It has been suggested at various times that the intermediates in the RAFT equilibria (**2** and/or **4**) might react reversibly with propagating radicals[26–28] and thus these species might be mediators of radical polymerization by a reversible termination mechanism.

A more recent finding is that certain thioketones (e.g. **5**) can act, albeit poorly, as control agents of radical polymerization.[29] The thioketones are proposed to act a spin-traps as shown in Scheme 2 and thus provide control by a reversible termination mechanism. RAFT agents (**1**), in particular those with poor leaving groups 'R', might, in principle, provide control over polymerization by similar chemistry. It is noteworthy that primary dialkyl trithiocarbonates are effectively inert in radical polymerization of styrene (with **51**)[30] and BA (with **59**).[31] This suggests that if or when radicals add to these trithiocarbonates, the intermediate formed undergoes no reactions other than rapid reversion to starting materials. There is no significant effect on the molecular weight distributions of the polymers formed in their presence.



Scheme 2.



Scheme 3.

Choice of RAFT Agents

A wide variety of thiocarbonylthio RAFT agents (ZC(=S)SR **1**) have been reported. A broad summary of these and the factors which influence choice of RAFT agent for a particular polymerization was presented in previous reviews.[1,4] The effectiveness of the RAFT agent depends on the monomer being polymerized and is determined by the properties of the free radical leaving group R and the group Z which can be chosen to activate or deactivate the thiocarbonyl double bond of the RAFT agent **1** and modify the stability of the intermediate radicals **2** and **4**. For an efficient RAFT polymerization (Scheme 1, Fig. 2):

- The initial RAFT agents **1** and the polymer RAFT agent **3** should have a reactive C=S double bond (high k_{add}).
- The intermediate radicals **2** and **4** should fragment rapidly (high k_β, weak S–R bond in intermediate) and give no side reactions.
- The intermediate **2** should partition in favour of products ($k_\beta \geq k_{-\mathrm{add}}$).
- The expelled radicals ($R^\bullet$) must efficiently re-initiate polymerization ($k_\mathrm{i} > k_\mathrm{p}$).

The properties of RAFT agents are often discussed in terms of the value of the equilibrium constants associated with radical addition to the thiocarbonylthio compound. Rates of addition are typically high ($\sim 10^6$–$10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$). Thus a high equilibrium constant generally implies a low fragmentation rate for the radical adduct and an increased likelihood for retardation and/or side reaction involving this species. Values of K do not, by themselves, provide sufficient information predict the ability of a RAFT agent to control polymerization.

In a given RAFT polymerization, there are at least four equilibrium constants that need to be considered.

- K_P ($= k_{\mathrm{addP}}/k_{-\mathrm{addP}}$) associated with the main equilibrium.
- K ($= k_{\mathrm{add}}/k_{-\mathrm{add}}$) and K_β ($= k_{-\beta}/k_\beta$) associated with the pre-equilibrium.
- K_R ($= k_{\mathrm{addR}}/k_{-\mathrm{addR}}$) associated with the reaction of the expelled radical with the initial RAFT agent (Scheme 3).

There may be other equilibrium constants to consider if penultimate group effects are significant (there are theoretical data[32,33] and some experimental evidence[34,35] to indicate

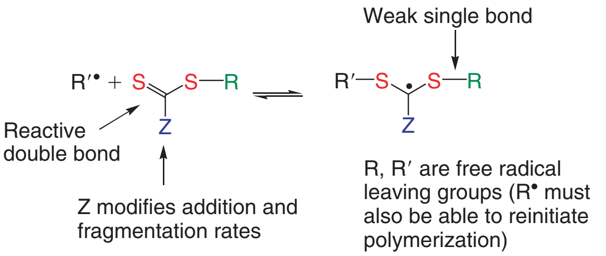
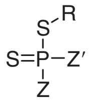


Fig. 2. Structural features of thiocarbonylthio RAFT agent and the intermediate formed on radical addition.

that this is the case). There are also a further series of reactions that need to be considered that involve initiator radical derived RAFT agents. In principle, RAFT agents of differing reactivity might be derived from each radical species present.

Values of K may estimated by determining the concentrations of the radical intermediates in RAFT polymerization by EPR (or ESR) spectrometry.[36–39] Buback and co-workers[37] have reported what they term the SP-PLP-ESR-RAFT technique where the rate of build-up and decay of the intermediate following radical generation is followed by EPR spectroscopy and analyzed to provide addition and (overall) fragmentation rates. Coote and co-workers[9,32,33,40–43] have devised methods for calculating absolute values of K by applying ab initio methods. Values of K have also been estimated on the basis of simulation of the polymerization kinetics.[44–46] However, most simulations have assumed a simplified RAFT mechanism in which K is assumed independent of the radical structure. Values of K estimated on the basis of the measured concentrations of the radical intermediates are much lower than those predicted by theoretical calculations.

On the basis of computational studies on RAFT agents, Z–C(=S)SR, a RAFT agent with Z = fluorine was proposed[40,43,47] as a 'universal' RAFT agent able to efficiently control the polymerization of both activated (e.g. acrylates, styrene) and less-activated monomers (e.g. vinyl acetate). The full utility of this class of RAFT agent has yet to be demonstrated experimentally. It has only been tested in styrene polymerization where limited control was observed (poor correspondence between found and calculated molecular weights, slightly narrowed polydispersity).[47] The utility of dithiophosphinate esters (**6**; Scheme 4) as RAFT agents[48] has been questioned on the basis of the results of computational studies.[49]



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Scheme 4.

Matyjaszewski and Poli[50] have reported the results of density functional theory (DFT) calculations used to estimate R–S bond dissociation energies in thiocarbonylthio RAFT agents (R–S(C=S)Z) and suggest these may be used as a guide for the design of RAFT agents. Even though some parallels might be expected, it should be pointed out that it is the bond dissociation energy of R–S bond in the radical intermediate (R–S(C($^\bullet$)–SR′)Z) rather than the RAFT agent (R–S(C=S)Z) that may be important in determining fragmentation rates (see Fig. 2). DFT calculations have also been applied in understanding the properties of radical adducts to phosphoryldithioacetates.[39] The suitability of DFT methods for calculations relating to RAFT polymerization has been questioned.[9,41]

The process of 'initialization', consumption of the initial low molecular weight RAFT agent, for styrene polymerization with cyanoisopropyl and cumyl dithiobenzoates at 70°C has been compared using in situ ^{1}H NMR measurements.[51] The rate-determining step was found to be the rate of addition of the expelled radical ($R^\bullet$) to styrene which was proposed to be faster for $R^\bullet$ = cyanoisopropyl than for $R^\bullet$ = cumyl. Existing literature suggests that the absolute rate constants for addition to styrene by the two radicals are similar.[52,53] However, the rate constants for cyanoisopropyl radical addition to RAFT agents is substantially lower than that for cumyl.[52] Molecular orbital calculations provide support for this finding.

A summary of 'new' RAFT agents and the polymerizations in which they have been applied is included in Tables 1–6. The Tables includes some RAFT agent/monomer combinations which provide poorer molecular weight control and/or polydispersity greater than 1.4. These are indicated by the monomer being in parentheses. Often these have been investigated in order to provide an understanding of the mechanism and to allow construction of guidelines for the choice of RAFT agent.

Dithiocarbamates, where the delocalization of the nitrogen lone pair into the thiocarbonyl group is minimized by electron-withdrawing substituents or by its being part of a conjugated system (e.g. **76**), are effective with styrenic and acrylic monomers. Recent work[54,55] has focussed on the

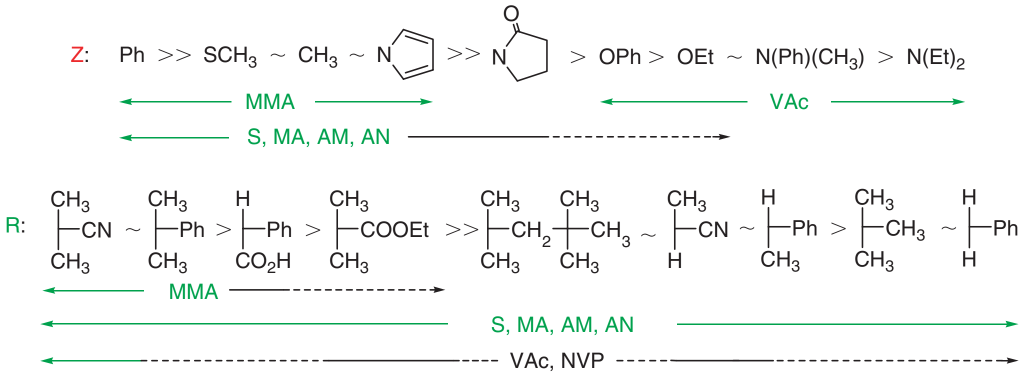


Fig. 3. Guidelines for selection of RAFT agents for various polymerizations.[4] For Z, addition rates decrease and fragmentation rates increase from left to right. For R, fragmentation rates decrease from left to right. Dashed line indicates partial control (i.e. control of molecular weight but poor polydispersity or substantial retardation in the case of VAc or NVP). For monomer abbreviations see footnotes to Table 1.

relative effectiveness of a series of dithiocarbamates where the nitrogen lone pair is part of a heteroaromatic ring system (**78**–**85**) in controlling polymerization of styrene. Of these, compounds **84** and **85**, where there is little delocalization of the lone pair into the aromatic system, were not effective as RAFT agents.

RAFT agents with R = phthalimidomethyl have been explored. The main instigation for this work was the synthesis of polymers with amine end-groups.[12,30,56] However, phthalimidomethyl radical is a good homolytic leaving group/initiating radical and can serve as a universal 'R' group in trithiocarbonate (**62** and **63** with S, BA, NIPAM) or xanthate RAFT agents (**73** with VAc, NVP) for monosubstituted monomers.

Secondary aromatic dithioesters with R = –CHPh(CN)[57] (**14**, **34**) and –CHPh(CO_2R) (e.g. **16**)[5,58] and analogous trithiocarbonates with R = –CHPh(CN) (**58**) have been shown to have utility in controlling polymerization of methacrylates. Results for RAFT polymerization with trithiocarbonate **58** are presented in Table 7. Both the dithioester **14**[57] and the methyl trithiocarbonate **58** (Table 7) give good molecular weight control and very narrow polydispersities. However, some retardation is evident with respect to similar polymerizations with tertiary cyanoalkyl RAFT agents, for example, methyl cyanoisopropyl trithiocarbonate,[59] under similar conditions. This may be indicative slow reinitiation by the phenylcyanomethyl radical though further study is required to establish this.

Fig. 3, taken from the previous review,[4] provides a general summary of how to select the appropriate RAFT agent for particular monomers. Note should be made of the dashed lines in the chart. Although some control might be achieved with these monomer RAFT agent combinations, the molecular weight distribution may be broad or they may be substantial retardation or prolonged inhibition. This proviso has been omitted in some representations of this data in the literature.

Vinylogous dithioesters, in which the thiocarbonyl and the free radical leaving group are separated by a conjugated unsaturated linkage (e.g. **90**–**93**; Table 8), are described in the patent literature[128] but little other than passing reference has appeared in the open literature.[129] A recent paper describes the synthesis and use of **90** and **91** as RAFT agents in polymerization of EA and styrene.[103] RAFT polymerizations in the presence of **90** or **92** should provide a three-armed star.

Synthesis of RAFT Agents

Arkema have commenced producing dibenzyl trithiocarbonate (**52**) on a pilot scale and have reported it as commercially available.[130] References containing syntheses of new RAFT agents by traditional methods are included in Table 1. Several papers that focus on RAFT agent synthesis are summarized in this section.

The use of thiocarbonylbisimidazole in the synthesis of RAFT agents was reported in the CSIRO patent.[128] Wood et al.[106] have now demonstrated the utility of this reagent in the synthesis of a range of trithiocarbonates, xanthates, and dithiocarbamates. Aoyagi et al.[131] have described conditions for synthesis of trithiocarbonates using minimal amounts of carbon disulfide.

A new 'one pot' synthesis of thiocarbonyl disulfides based on the reaction of a thiol with *p*-toluenesulphonyl chloride (TsCl) has appeared.[132] The proposed mechanism for the process is shown in Scheme 5. A further example of the synthesis of a tertiary trithiocarbonate (**50**) from the thiocarbonyl disulfide has been published.[12]

Two types of reagent (**36**[94] and **37**[95]; Scheme 6) have been reported for conversion of amine functionality in polymers/surfaces to RAFT agent functionality.

Attempted RAFT polymerization of MA or styrene agent with phenyldithioacetic acid meets with limited success.[96] However, the RAFT agent formed by Markovnikov addition of phenyldithioacetic acid (**88**) to styrene (formed by preheating a solution of the dithioacid in styrene at 70°C for 24 h) can be used directly in styrene polymerization without need for isolating the RAFT agent.[96] This strategy cannot be applied with electron deficient monomers which react with dithioacids by an anti-Markovnikov Michael-type addition.

Primary and secondary trithiocarbonates are simply made by reaction of the trithiocarbonate salt with an alkylating agent. For example, cyano(phenyl)methyl methyl trithiocarbonate (**58**) is synthesized as follows.[60] A solution of 2-bromo-2-phenylacetonitrile (1.1 g, 5.5 mmol) in ethyl acetate (10 mL) was added dropwise to a stirred suspension of sodium methyl trithiocarbonate (0.7 g, 5 mmol) in ethyl acetate (10 mL) and the mixture was stirred for 12 h and poured into water (20 mL). The aqueous layer was extracted with ethyl acetate, dried with $MgSO_4$, filtered, and the solvent removed. The residue was purified by column chromatography on silica using 10% ethyl acetate in petroleum spirits to afford the title compound (0.82 g, 69%. δ_H 2.8 (3H, CH_3), 6.2 (1H, CH), 7.2–7.6 (5H, ArH)).

The trithiocarbonate salt can be formed in situ from the thiol and carbon disulfide with triethylamine as base (e.g. in the synthesis of **62** and **64**).[30]

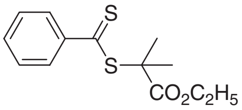
Characterization of RAFT-Synthesized Polymers

Most papers on RAFT polymerization contain information on the characterization of RAFT-synthesized polymers and/or the RAFT process. We consider here papers where the characterization of RAFT-synthesized polymers by spectroscopic or chromatographic methods is a primary focus.

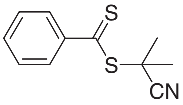
Protic end groups in RAFT-synthesized (and other) polymers can be determined by derivatization with trichloroacetyl isocyanate and ^1H NMR analysis.[133] The method is effective and quantitative for hydroxy, amino, and carboxy chain ends. However, some difficulties were encountered and the method appears non-quantitative for thiol end groups. Two-dimensional chromatography techniques have been applied to characterize end-functional PMMA[109,134] and PBA[109] synthesized by RAFT polymerization.

It has been reported that oxidation of the thiocarbonylthio group by tetrahydrofuran-derived peroxides can cause problems when tetrahydrofuran is used in sample preparation for mass spectrometry.[135]

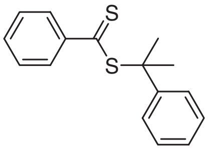
Table 1. RAFT agents and RAFT polymerizations—aromatic dithioester RAFT agents[A,B]



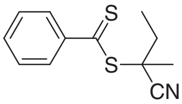
7* CMS/NMPI[61] S/VBSC[62]



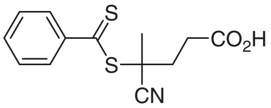
8* AN[63] (DBI)[64] DMAEMA[65] HPMAM/NMS[66] *MMA*[67]



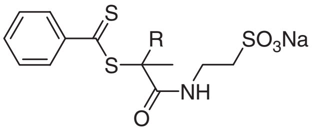
9* (DBI)[64] DMAEMA[68] GMA[68] HEMA[68] (MA)[69] MMA[46,70,71] NIPAM[72] PFMA[73] (S)[44,74] S[75] *S*[76] S/AN[68] S/MAH[68]



10* EEA[77] BMA[78] BzA[78] BzMA[78] DMAEMA[78] EHA[78] MA[78] MMA[78,79] tBA[78]

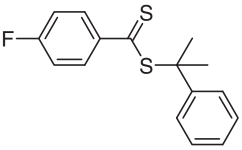


11* (DBI)[64] DMA[72] HPMAM[80] *MMA*[81] PEGMA[72] PFMA[73] *S*[81] XMA[82]

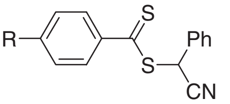


12a* $R = H$

12b $R = CH_3$[83] AM[83] TMAEMA[83]



13 MMA[71]

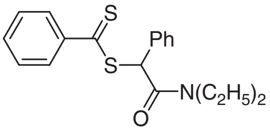


14a $R = H$[57] AcS BA MMA tBA S[57]

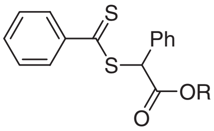
14b $R = OCH_3$[57] S BA MMA[57]

14c $R = F$[57] BA[57]

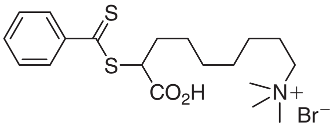
14d $R = Ph$[57] BA[57]



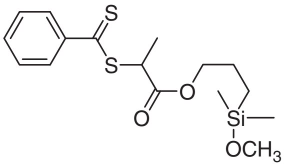
15[84] DMA MA S[84]



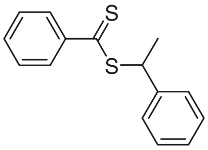
16* $R = CH_3$ (DBI)[64]
$R =$ PEG MMA[58]



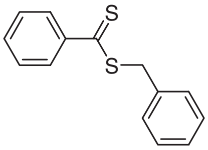
17[85] S[85]



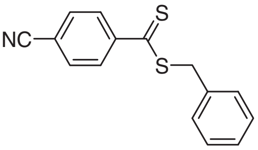
18[86]



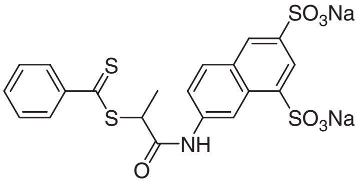
19* (*S*)[74]



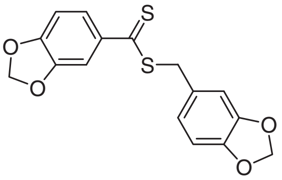
20* (MA)[87] NAPM[88] (*S*)[74]



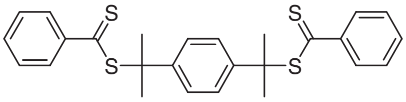
21 (MA)[87]



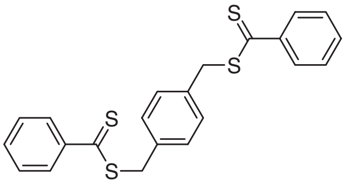
22[83] PEGA[72,83] SSO_3Na[72]



23[89] S[89]

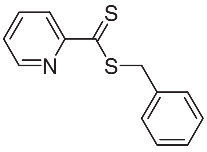
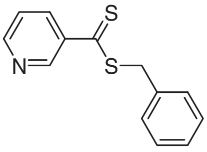
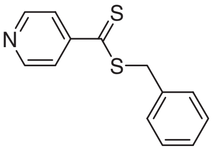
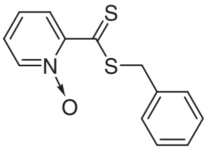
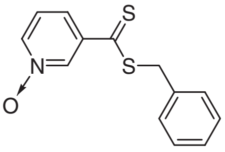
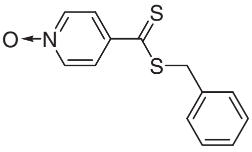
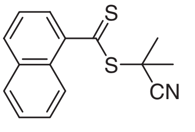
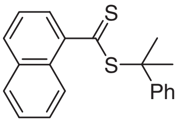
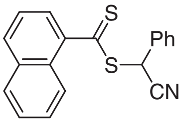
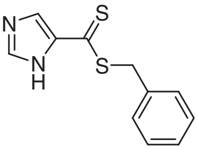
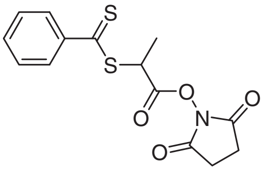
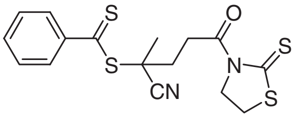


24*[90] LMA MMA[90]



25*[90] S[90]

Table 1. *Continued*

 **26**[38] S[38]	 **27**[38] S[38]	 **28**[38] S[38]
 **29**[38] (S)[38]	 **30**[38] (S)[38]	 **31**[38] (S)[38]
 **32*** MMA[91,92]	 **33*** MMA[92]	 **34**[57] S BA MMA[57]
 **35**[93] NIPAM[93]	 **36**[94],C	 **37**[95],C

[A] First reference after compound number (where given) provides a synthesis of the RAFT agent. An asterisk indicates the RAFT agent is mentioned in our previous review or has been previously described.[4] If a monomer appears in italics the polymerization was performed in heterogeneous media (emulsion, miniemulsion). If a monomer appears in parentheses relatively poor control was reported (usually manifest as a broad molecular weight distribution (PDI > 1.4) and/or significant retardation/inhibition).

[B] Abbreviations: AcS, 4-acetoxystyrene; AA, acrylic acid; AN, acrylonitrile; BA, butyl acrylate; CMS, chloromethylstyrene; DA, dodecyl acrylate; DBI, dibutyl itaconate; DMA, *N,N*-dimethylacrylamide; DMAEA, 2-(dimethylamino)ethyl acrylate; DMAEMA, 2-(dimethylamino)ethyl methacrylate; EA, ethyl acrylate; EAA, ethyl α-acetoxyacrylate; EEA, ethoxyethyl acrylate; EVC, *N*-ethyl-3-vinylcarbazole; GMA, glycidyl methacrylate; HEA, 2-hydroxyethyl acrylate; HEMA, 2-hydroxyethyl methacrylate; HPMAM, *N*-hydroxypropyl methacrylamide; LMA, dodecyl methacrylate; MA, methyl acrylate; MAH, maleic anhydride; MMA, methyl methacrylate; NAPM, *N*-acryloyl-L-proline methyl ester; NAP, *N*-acryloylpyrrolidine; NAS, *N*-acryloyloxysuccinimide; NIPAM, *N*-isopropylacrylamide; NPMI, *N*-phenylmaleimide; NMS, *N*-methacryloyloxysuccinimide; NVP, *N*-vinylpyrrolidone; PEG, poly(ethylene glycol) monomethyl ether; PEGA, poly(ethylene glycol) monomethyl ether acrylate; PEGMA, poly(ethylene glycol) monomethyl ether methacrylate; PFMA, pentafluorophenyl methacrylate; S, styrene; SSO_3Na, sodium styrene-4-sulphonate; TPSM, 3-(trimethoxysilyl)propyl methacrylate; tBA, *tert*-butyl acrylate; TMAEMA, 2-(trimethylamonium)ethyl methacrylate; VAc, vinyl acetate; VBSC, vinylbenzenesulphonyl chloride; XA, functional acrylate; XMA, functional methacrylate.

[C] Compounds not used as RAFT agents directly but served as precursors to other RAFT agents.

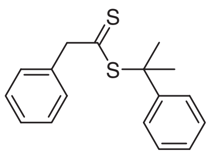
Size exclusion chromatography coupled to electrospray ionization mass spectrometry has been used to characterize RAFT-synthesized PMA.[136] The work is described below under Side Reactions in RAFT. GPC coupled with UV detection has been used to determine the butyl trithiocarbonate and phthalimidomethyl ends groups of PBA prepared with RAFT agent **62**.[56] This and ^{13}C NMR was used to estimate the extent of short- and long-chain branching in PBA as a function of conversion. Capillary zone electrophoresis has been recommended as the method of choice for characterizing RAFT-synthesized PAA oligomers.[137]

Polymerization Kinetics

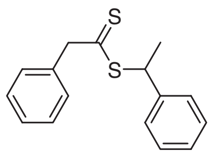
Kinetic simulation is frequently used as a tool to correlate experimental data with theoretical models. New approaches to kinetic simulation of RAFT polymerization using Monte Carlo methods in solution[138] or emulsion[139] have been reported. Monteiro and co-workers have applied kinetic simulation to study various aspects of RAFT polymerization[15,140,141] including block copolymer synthesis[140] and the synthesis of polymers using bis-RAFT agents.[141] They used a method of moments to solve simplified sets of differential equations using *MATLAB*.

RAFT polymerization and kinetic simulation with *Predici* have been applied to determine chain-length dependent termination rate constants in radical polymerizations[70,99–101,121,142,143] of various monomers including MA (with **40**[99,143] or **66b**[143]), BA (with **40**[100] or **66a**[116]), DA (with **40** or **66b**[101]), MMA (with **9**[70]), and VAc (with **70b**[121]). Most experiments[70,99,100,121] involve collecting

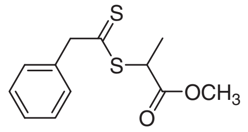
Table 2. RAFT agents and RAFT polymerizations—dithioester RAFT agents[A]



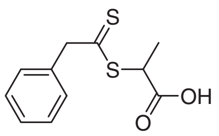
38* (DBI)[64] *S*[76]



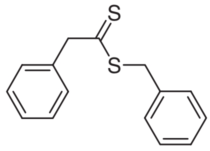
39* MA[96] (NVP)[97] S[96] (*S*)[98]



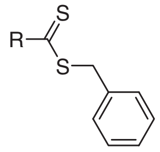
40* MA[99] BA[100] DA[101]



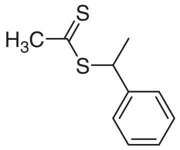
41* NIPAM[102]



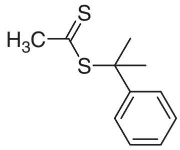
42*[72] MA[87] XA[72]



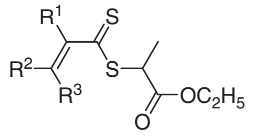
43a* R = CH_3 *S*[74]
43b R = C_2H_5 MA[87]



44* S[34]



45* MMA[34]



46[103] EA S[103]
46a $R^1 = H, R^2 = R^3 = CH_3$
46b $R^1 = R^2 = H, R^3 = Ph$
46c $R^1 = R^2 = R^3 = Ph$

[A] See footnotes [A,B] of Table 1.

rate of polymerization data from RAFT polymerization as a function of conversion. The quality of the data are dependent on the assessment of the importance of other chain length and conversion dependent process (the RAFT equilibria, initiator efficiency, propagation, chain transfer to monomer/polymer) and the extent to which the variations in the observed rate of polymerization with conversion can be attributed to the chain-length dependence of the termination rate constant. A more recent variant on this approach for determining chain-length dependent termination rate constants makes use of single-pulse pulsed laser polymerization (SP-PLP).[100,116]

Peklak et al.[46] have used numerical simulation to model RAFT polymerization of MMA with cumyl dithiobenzoate and study the effects of diffusion (the gel effect). Free volume theory was applied to estimate effect of diffusion on the various reaction steps including the RAFT equilibria, initiator efficiency, and bimolecular termination. A very good correlation with experimental data was obtained.

Side Reactions in RAFT Polymerization

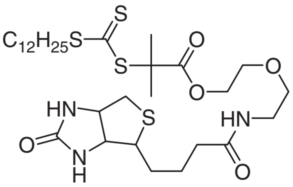
A variety of side reactions can potentially complicate the RAFT mechanism causing retardation, byproducts and anomalies in the molecular weight distributions. Whether these occur depends on the particular RAFT agent/monomer combination and the reaction conditions. There remains some controversy surrounding the stability and possible alternate fates of the intermediate radical in RAFT polymerization. The current (mid 2006) status with respect to dithiobenzoate RAFT agents has been summarized.[25]

A detailed study of the product of RAFT polymerization of MA with both cumyl dithiobenzoate and cumyl dithiophenylacetate using coupled size exclusion chromatography–electrospray ionization mass spectrometry has been carried out with a view to detecting products which might be formed by a side reaction of the intermediate radical by radical–radical termination. As in previous studies of this nature, these were not detected.[136]

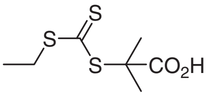
Buback and Vana[144] have proposed a new mechanism for disappearance of the product of intermediate radical termination during RAFT polymerization with dithiobenzoates. In that it does not lead to byproducts and the proposal has the potential of resolving the current impasse re the mechanism of retardation observed in these polymerizations.[25] The proposed mechanism involves the intermediate radical termination (**95** or an isomer) reacting with a propagating radical to regenerate the intermediate **94** and produce **96** (identical to the normal product of radical–radical termination) as the only byproduct. While the process is thermodynamically favourable being driven by aromatization and formation of a relatively stable radical, there appears no literature precedent for the reaction of quinonoid species such as **95** with radicals to proceed as shown in Scheme 7.

Another possibility is that the quinonoid species **95**, if formed, reacts with radicals by hydrogen atom transfer. This process would result in formation of a new intermediate **97** to fragment to a new RAFT agent **99** and a dead polymer chain **98** (Scheme 8). Quinonoid species are well known as excellent hydrogen atom donors. The effect on kinetics would be similar to the Buback–Vana proposal[144] but would lead to the formation of a new RAFT agent **99** which might be detectable under appropriate conditions but, for the case of acrylate polymerization, may not be readily distinguished

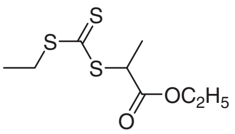
Table 3. RAFT agents and RAFT polymerizations—trithiocarbonate RAFT agents[A]



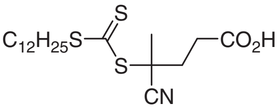
47[104] HPMAM[104] NIPAM[104]



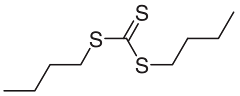
48 DMA[105]



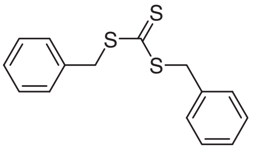
49[106] MA[106]



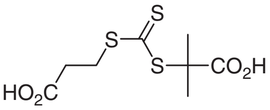
50[12] MMA[4,12]



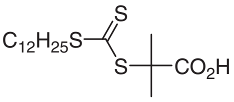
51[30] (S)[30]



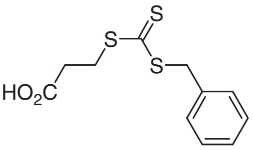
52*[106] AA[107] AN[108] MA[106]



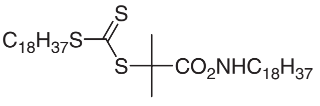
53[31] BA[31]



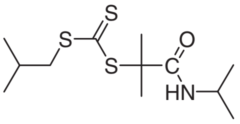
54* BA[31] MA[71] MMA[109]



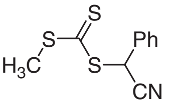
55[31] AA[110] BA[31] NIPAM[110]



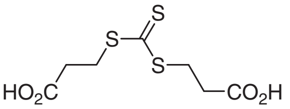
56[111] NIPAM[111,112]



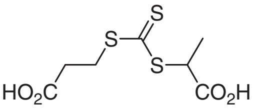
57[111] NIPAM[111]



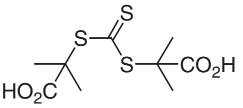
58 MMA[B]



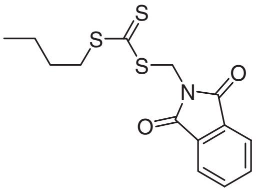
59[31] (BA)[31]



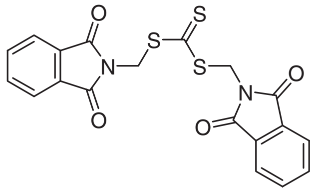
60[31] BA[31]



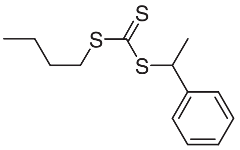
61* AA[110] BA[31,109] MA[71] NIPAM[110]



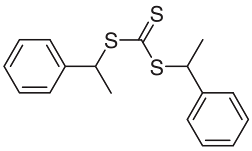
62[30] BA[56] NIPAM[56] (NVP)[56] S[12,30,56]



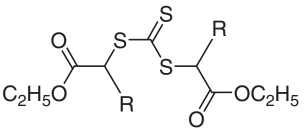
63[30] S[30]



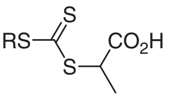
64[30] S[30] ODA[113,114] ODA/NVP[113,114] ODA/MAH[113,114]



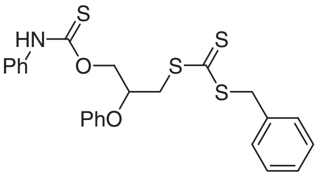
65* AA[115]



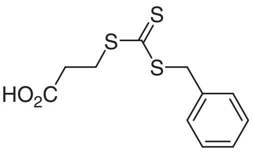
66a* $R = C_2H_5$ BA[116]
66b $R = CH_3$ DA[101]



67a $R = C_4H_9$[117] AA[117]
67b $R = C_{12}H_{25}$[117] AA[117]



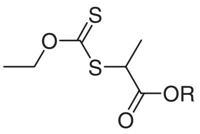
68[118] S[118]



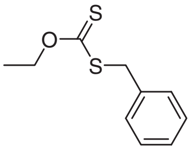
69 AA[110] HEMA/S[119] NIPAM[110]

[A] See footnotes A,B of Table 1. [B] The synthesis (see section Synthesis of RAFT Agents) and results obtained using RAFT agent **58** (Table 1) are provided in this paper.

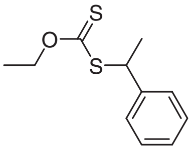
Table 4. RAFT agents and RAFT polymerizations—xanthate RAFT agents[A]



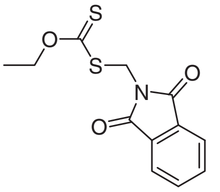
70a*[106] $R = C_2H_5$ MA[106]
70b* $R = CH_3$ AA/EAA[120] (EAA)[120]
BA/EAA[120] DMA/EAA[120]
DMAEA/EAA[120] VAc[121]



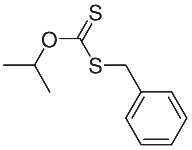
71*[97] NVP[97]



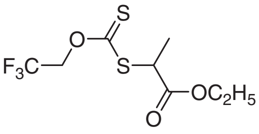
72*[97] NVP[97] (*S*)[98]



73[56] NVP[56] VAc[56]



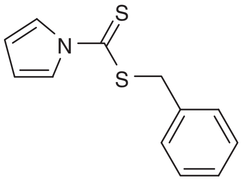
74*[106] VAc[106]



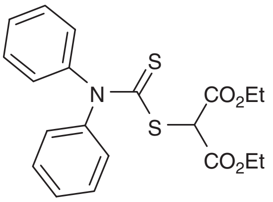
75a* *S*[122]

[A] See footnotes [A,B] of Table 1.

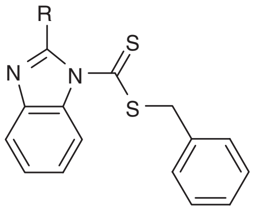
Table 5. RAFT agents and RAFT polymerizations—dithiocarbamate RAFT agents[A]



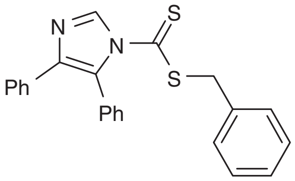
76* EVC[123]



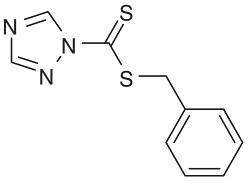
77* NVP[124]



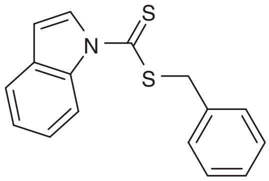
78[54] S[54]
78a $R = CH_3$
78b $R = Ph$



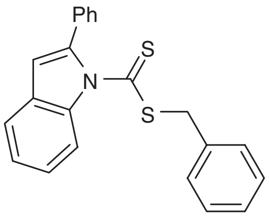
79[55] S[55]



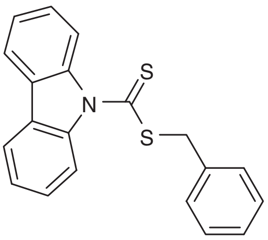
80[55] S[55]



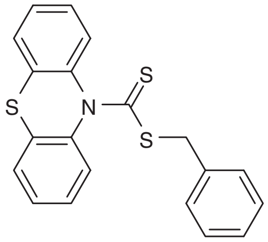
81[55] S[55]



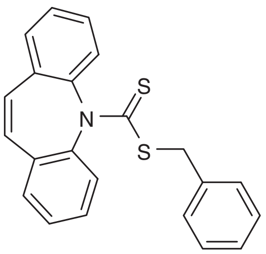
82[55] S[55]



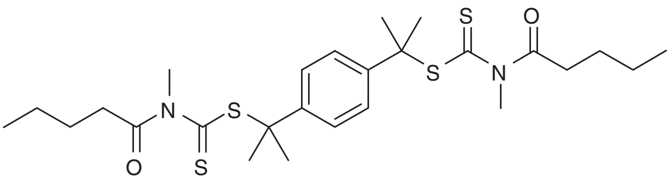
83[55] S[55]



84[55] (S)[55]



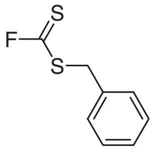
85[55] (S)[55]



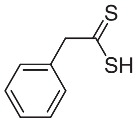
86[125] BA MA/MAA[126]

[A] See footnotes [A,B] of Table 1.

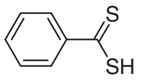
Table 6. RAFT agents and RAFT polymerizations—other RAFT agents[A]



87[47] S[40,47]



88* (MA[96] S[96])



89* MMA[127]

[A] See footnotes [A,B] of Table 1.

Table 7. Molecular weights obtained in RAFT polymerization[A] of MMA with methyl phenylcyanomethyl trithiocarbonate 58[60]

$[RAFT]_0$ [M]	Time [h]	$\overline{M}_n$[B] [g mol^{-1}]	$\overline{M}_n$ (calc)[C] [g mol^{-1}]	$\overline{M}_w/\overline{M}_n$	Conv[D] [%]
0.011	4	6600	5900	1.26	9
0.011	8	22100	26700	1.13	42
0.011	16	53400	60000	1.09	>95
0.056	16	5200	5600	1.16	43
0.056	24	7400	8700	1.13	67
0.056	64	12100	12200	1.09	>95

[A] MMA 75% (v/v) in benzene with azobis(isobutyronitrile) initiator (0.0071 M), 60°C. [B] $\overline{M}_n$ in polystyrene equivalents. [C] $\overline{M}_n$ (calc) $\sim [MMA]_0/[RAFT]_0 \times$ conv $\times\ 100.15 + 238.99$. [D] Gravimetric conversion of monomer to polymer.

from the byproduct formed by the process mentioned in the paragraph below (Scheme 9).

The above processes (Schemes 7 and 8) are only relevant to RAFT polymerizations with dithiobenzoates and closely related RAFT agents. They are not relevant to RAFT polymerizations carried out with trithiocarbonates, aliphatic dithioesters, and most other RAFT agents, many of which also give retarded polymerization.

Bimodal molecular weight distributions are often observed in RAFT polymerization of acrylate monomers when polydispersities are less than 1.2.[145] Bimodal distributions have been observed for dithiobenzoate, dithioacetate, trithiocarbonate, and dithiocarbamate RAFT agents. They are manifest as a higher molecular weight shoulder with peak molecular weight approximately twice that of the parent peak and are most pronounced for higher conversion and higher molecular weight polymers. Postma et al.[56,113] have provided evidence that the mechanism of formation is copolymerization of the macromonomer formed by the propagating radical undergoing backbiting β-scission (Scheme 9). The incidence of long chain branching by this mechanism was compared to that of short chain branching (by backbiting followed by propagation). Because β-scission competes with propagation the number of branches per molecule is greater for high monomer conversions and for higher molecular weights. Note that the proposed process does not depend on RAFT mechanism and should complicate all radical polymerizations of acrylate monomers. The process may also complicate the polymerizations of other monosubstituted monomers (e.g. VAc) but is likely to be less prevalent because other monomers generally display a reduced propensity for backbiting β-scission.

Further studies of RAFT polymerization in the presence of dithioacids (**88**, **89**) have been reported.[96,127] These polymerizations are characterized by a prolonged inhibition period during which a RAFT agent is formed followed by normal RAFT polymerization. The efficiency of conversion of the dithioacid to the RAFT agent can be low and a variety of side reactions are proposed to occur to complicate the process.[96,127]

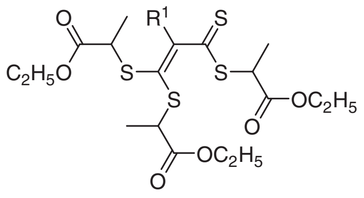
Reaction Conditions (Initiator, Temperature, Pressure, Solvent, Lewis Acids)

A further study of UV-initiated RAFT polymerization of MA (with **54** or **61**) and MMA (with **9** or **13**) with added photoinitiator has been reported.[71] The paper emphasizes the importance of selecting an irradiation wavelength, the RAFT agent, and the photoinitiator (2,4,6-trimethylbenzoyl)diphenylphosphine oxide, to avoid side reactions such as photodissociation of the RAFT agent.[71] Gamma-initiated RAFT polymerizations of MA in the presence of various dithioesters (including **20**, **21**, **42**, **43b**),[87] xanthates[146] and dithiocarbamates,[147] of MMA in the presence of **32**,[91] and of NIPAM and AA in the presence of **55** or **61** in aqueous media[110] have been reported.

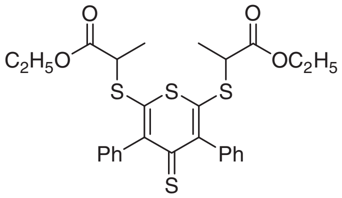
In the previous review we reported experiments on the influence of oxygen and degassing on the outcome of MMA polymerization.[4] Thermally initiated (no added initiator at 80°C) RAFT polymerization of MMA with **32** or **33** in the presence of oxygen provided high molecular weight polymer and remarkably good control.[92] The proposed mechanism involves formation of P(MMA-*co*-oxygen).

RAFT polymerization of MA in supercritical carbon dioxide with cumyl dithiobenzoate showed substantially greater retardation than when toluene was used as solvent.[69] RAFT polymerization of NVP in fluoroalcohols with xanthates (**71** or **72**) was carried out to achieve some stereochemical control over propagation. An increase in syndiotactic dyads from 52

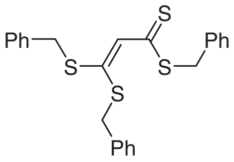
Table 8. Vinylogous dithioester RAFT agents[A]



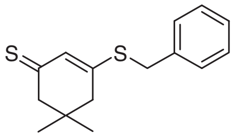
90[103] S[103]



91[103] S[103]



92[128] S[128]



93[128] S[128,129]

[A] See footnotes A,B of Table 1.

to ~62% for polymerization of NVP in perfluoro-*t*-butanol solvent at 20°C.[97] An inhibition period was observed which might be attributed to a poor choice of 'R' (benzyl or 2-phenylethyl) for the xanthate RAFT agents.

RAFT polymerization is compatible with the presence of Lewis acids which can be used to influence tacticity of homopolymers and/or the tendency for alternation in copolymerization.[4] Further studies of the use of rare earth metal triflates to control the stereochemistry of polymerization of acrylamide derivatives have been reported (NIPAM,[148] amino acid derived acrylamide derivatives, *N*-acryloyl-L-phenylalanine methyl ester[149]). Studies on (alternating) copolymerization include styrene with MMA[150] and β-pinene with acrylonitrile.[151]

The RAFT polymerization of a cyclodextrin–styrene host–guest complex in water has been studied.[152] Molecular weights and polydispersity were controlled by the RAFT process, however, molecular weights are higher and polydispersities broader than observed for solution or bulk polymerization of styrene with the same RAFT agent. Loss of control was associated with precipitation of the polymer.

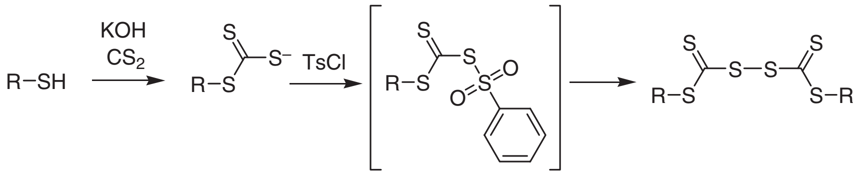
There have been further studies relating to the hydrolytic stability of RAFT agents in aqueous media.[82,83] Better results were obtained when sodium bicarbonate as opposed to carbonate was used to neutralize and solubilize the acid functional dithiobenzoate RAFT agent **11** used for control of polymerization of a glycopolymer methacrylate.[82] The effect may be related to the need to control the pH of the reaction medium particularly when using dithiobenzoate RAFT agents in aqueous media.

Arita et al.[75] have reported high temperature (up to 180°C), high pressure (1000 bar) RAFT polymerization of styrene with cumyl dithiobenzoate **9**. The conditions provided improved control (attributed to a higher fragmentation rate of the RAFT intermediate) and RAFT agent decomposition was not detected (compare below).

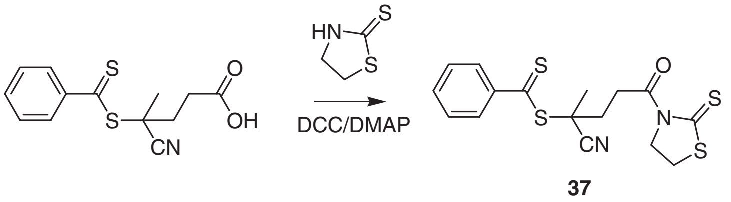
There have been several studies on the thermal stability of RAFT agents and RAFT-synthesized polymers and the possible influence of this on the outcome of RAFT polymerization. Cumyl dithiobenzoate **9** appears substantially less stable than benzyl or phenylethyl dithiobenzoate and degrades rapidly at temperatures over 100°C.[153] The instability was attributed to reversible formation to AMS and dithiobenzoic acid. The success of high temperature polymerization (of, for example, styrene) was attributed to the fact that the RAFT agent **9** was rapidly consumed and converted to more stable polymeric RAFT agents. It was also reported that the poor control in synthesis of PMMA with dithiobenzoate RAFT agents at higher temperatures (120°C) could be attributed to the lability of the dithiobenzoate end group.[154] Other work (see later discussion on end group transformation), while confirming that thermolysis is a suitable method for end group removal, indicates that dithiobenzoate end groups of RAFT-synthesized PMMA are stable to much higher temperatures.

The effect of impurities in cumyl dithiobenzoate on RAFT polymerization of HEMA, styrene, and MA has been studied.[155] Significant retardation manifest as an inhibition period was observed with samples that had not been rigorously purified by HPLC or which had been stored for a short time (<3 months) under refrigeration at −20°C. Samples purified by column chromatography on silica gave a significant inhibition period even when used immediately following purification. Dithiobenzoic acid was considered as a likely impurity.[155] Actual impurities in cumyl dithiobenzoate will depend on how it was synthesized and stored. We have found that cumyl dithiobenzoate purified by column chromatography on *alumina* with hexane as eluant and stored at 4°C for some years in the absence of light remains very effective.[156] Another potential impurity in dithiobenzoate RAFT agents is bis(thiobenzoyl)disulfide. This may form from cumyl dithiobenzoate on exposure to light and such disulfides are known to inhibit polymerization until consumed by reaction with initiator-derived radicals.[157,158]

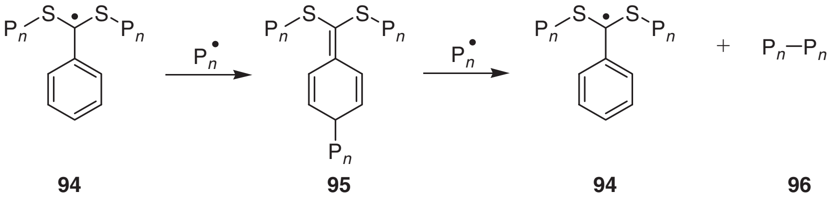
Schubert and co-workers[77–79,119,159,160] have reported on the development and application of high-throughput techniques in developing conditions for RAFT polymerization of various (meth)acrylate and for characterization of the synthesized polymers. The methods were used to study RAFT



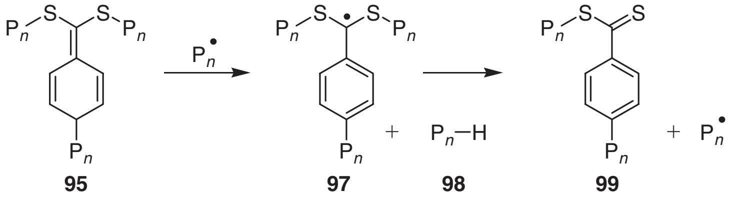
Scheme 5.



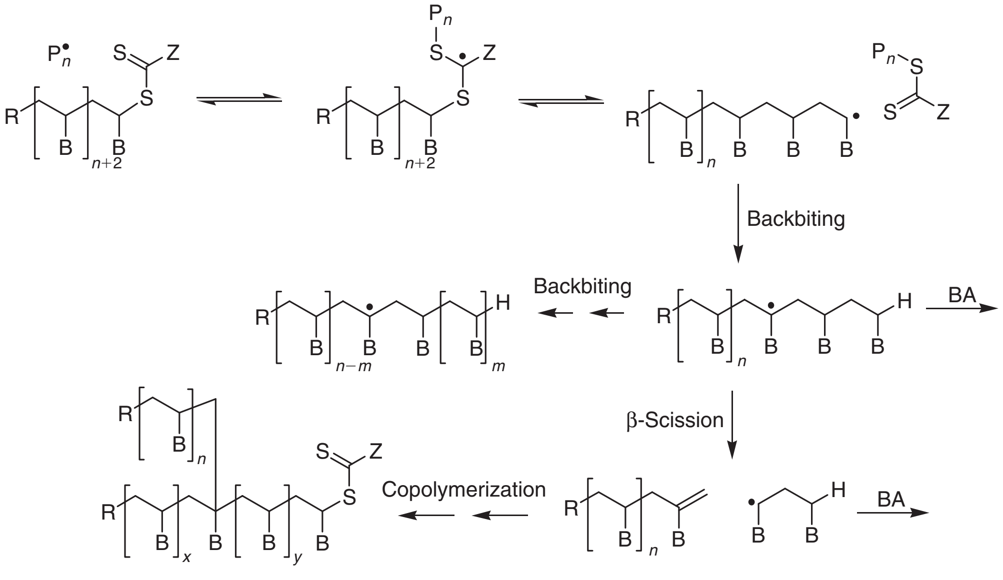
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9. B = $CO_2C_4H_9$.

polymerization of 2-ethoxyethyl acrylate,[77] a protected form of acrylic acid.

RAFT Polymerization in Heterogeneous Media

A large number of recent studies relate RAFT polymerization in heterogeneous media (emulsion,[67,74,81,98,117,122,139,161–166] miniemulsion,[10,76,167–175] or suspension[176]). The area has been reviewed by McCleary and Klumperman[11] and Save et al.[177]

'Surfactant free' emulsion polymerization making use of a hydrophilic macroRAFT agent (typically based on PAA oligomer formed with RAFT agent **67**)[117,161,163,164] has been used for BA[117] and styrene.[163,164] Gilbert[164] has proposed a simple theoretical model for particle formation by self assembly during RAFT emulsion polymerization and has applied this to analyze data for styrene polymerization.

A study of the surfactant (polymerizable surfmers and classical) in RAFT miniemulsion polymerization of styrene and MMA with **11** has been carried out.[81] Bimodal molecular weight distributions were obtained when surface-active monomers were used.

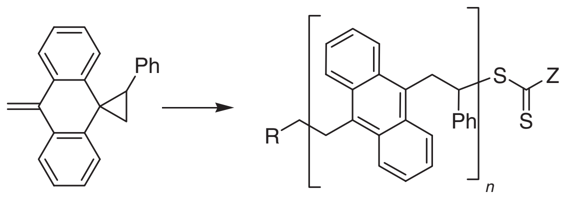
For batch MMA polymerization in emulsion with cyanoisopropyl dithiobenzoate **8** higher surfactant levels and initiation rates were found to improve colloidal stability.[67] Hartmann et al.[98] have studied the effect of degassing on latex stability in RAFT emulsion polymerization of styrene with dithiophenylacetate **39** (bimodal distribution) or xanthate **72** (broad distribution but good control). They report that the use of surfactant-free polymerization media degassed through freeze–pump–thaw cycles provides stable emulsions whereas nitrogen degassing does not.

Tauer and co-workers[74,166] have examined RAFT agent concentrations in the aqueous and monomer phase and the diffusion rate of RAFT agents from the monomer to the particle phase for styrene emulsion polymerization with various dithiobenzoate (**9**, **19**, **20**) and dithioacetate (**43**) RAFT agents. They also provided evidence that particle entry by initiator-derived radicals, including charged species such as sulfate radical anion, can take place without monomer addition. This result appears at odds with theory that suggests that aqueous phase oligomerization (*z*-mer formation) occurs before particle entry. Even though RAFT agents are rapidly oxidized by sulfate radical anion this appears not to be a significant side reaction in peroxydisulfate-initiated RAFT emulsion polymerization.[74]

The preparation of liquid-filled (isooctane core) polystyrene nanocapsules by RAFT miniemulsion polymerization has been reported.[76] Although good control over polymerization was obtained with both cumyl dithiobenzoate **9** and dithiophenylacetate **38**, significant retardation was observed with the dithiobenzoate RAFT agent and it was proposed this prevented development of the desired core–shell morphology.

RAFT Polymer Syntheses

Polymer syntheses by RAFT polymerization are summarized in Tables 1–6 and 8; only systems which require separate comment are mentioned here or in subsequent sections.



100

Scheme 10. R = PHCH$_2$, Z = Ph or pyrrole.

Several papers report on the synthesis of glycopolymers by RAFT polymerization of acrylamide,[178] vinyl ester,[179] or methacrylate[82,180,181] derivatives of glucose or lactose. Relatively broad polydispersities ($\overline{M}_w/\overline{M}_n \sim 1.5$–3) were obtained in RAFT polymerization of itaconate esters (e.g. DBI) using RAFT agents known to be suitable for methacrylate esters (e.g. **8**, **9**, **11**).[64]

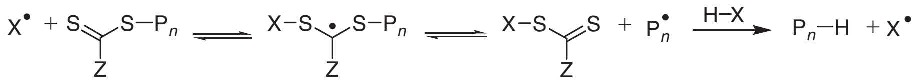
RAFT ring-opening polymerization on monomer **100** provided a polymer with anthracene units as part of the backbone (Scheme 10).[182]

End-Functional Polymers and End-Group Transformations

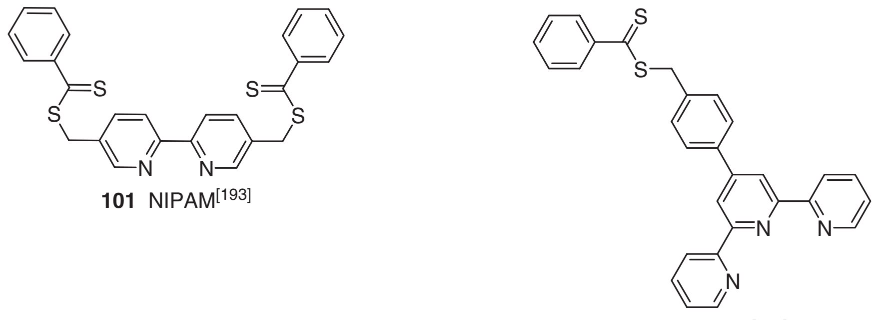
Processes for thiocarbonylthio end group removal-transformation post RAFT polymerization have attracted significant interest.[12,30,66,183–185]

Free radical reducing agents can be used to replace the thiocarbonylthio group with hydrogen. These reducing agents comprise a free radical source and a hydrogen atom donor such as tributylstannane,[12,30] tris(trimethylsilyl)silane,[30] hypophosphite salts,[183] or isopropyl alcohol[186] and reduction takes place by a free radical chain reaction for which the propagation steps are shown in Scheme 11. An efficient hydrogen atom donor is required to limit side reactions such as reactions between the radical species, which may be manifest as the development of a bimodal molecular weight distribution. Tri-*n*-butylstannane is one of the most effective hydrogen atom donors but its use is complicated by the formation of byproducts which are potentially toxic and may be difficult to remove. The use of tris(trimethylsilyl)silane was explored for the reduction of butyl trithiocarbonate end groups of polystyrene.[30] However, formation of product with a bimodal molecular weight distribution indicates inefficient trapping of radicals.[30] Hypophosphite salts were demonstrated to be effective reducing agents for dithiobenzoate and trithiocarbonate (and most likely other thiocarbonylthio) end groups of acrylic and styrenic polymers and the byproducts or reduction are innocuous and readily removed.[183]

Perrier[184] reported that the thiocarbonylthio end groups could be removed from a wide range of RAFT-synthesized polymers by heating the polymer with a large excess of a radical initiator (typically AIBN) with respect to the end groups. Incomplete end group removal (~95%) reaction was observed for polystyrene with trithiocarbonate ends[30] but the process is effective for HPMAM/NMS with dithiobenzoate ends.[66]



Scheme 11. H–X is a hydrogen atom donor.



101 NIPAM[193]

102 NIPAM S[193]

Scheme 12.

Thermolysis provides another method for thiocarbonylthio group removal.[12,30,56,187,188] Butyl trithiocarbonate groups are cleaved from RAFT-synthesized polystyrene[12,30,187] and PBA[56,187] by heating at ~180°C in the absence of air. The dominant mechanism of end group loss depends on the particular polymer, involving concerted elimination (Chugaev process)[189,190] in the case of polystyrene and initial C–S bond homolysis in the case of PBA. Thermogravimetric analysis (TGA) of PMMA with dithiobenzoate end groups has been reported by Lima et al.,[109] Patton et al.,[90] Xu et al.,[154] and Chong et al.[188] TGA of PMMA with methyl trithiocarbonate end groups has been reported by Chong et al.[188] Loss of the PMMA dithiobenzoate end appears to involve a concerted elimination reaction. Loss of the methyl trithiocarbonate end involves C–S bond homolysis.

The thermolysis of xanthate-terminated polymers has also been reported.[56,191] For the case of both *S*-polystyrene and *S*-poly(*t*-butyl acrylate) *O*-isobutyl xanthate, the reported mechanism involves selective elimination to provide 2-butene and a polymer with a thiol end group.[191] In contrast, for the case of *O*-ethyl *S*-poly(vinyl acetate) xanthate,[56] the products are consistent with involvement of the poly(vinyl acetate) (PVAc) propagating radical and suggest a mechanism involving initial C–S bond homolysis.

The transformation of thiocarbonylthio groups to thiol end groups is often complicated by side reactions.[12,90,109,185] Bimodal molecular weight distributions are thought to arise by oxidative coupling (disulfide formation). The problem can be mitigated by reduction of the disulfide in a subsequent process (e.g. with Zn/CH_3CO_2H[12,192] or tris(2-carboxyethyl)-phosphine)[185]). Thus, borohydride reduction of PNIPAM with trithiocarbonate ends gave a product (with a monomodal which was treated with tris(2-carboxyethyl)phosphine to provide the same polymer with thiol ends).[185] The thiol ends were reacted with *N*-(1-pyrenyl)maleimide to attach a fluorescent label.

Thiols can also be produced directly by performing aminolysis in the presence of a small amount of a reducing agent (e.g. sodium bisulfite, $Na_2S_2O_4$[90,109]). Thiols so formed may be transformed to sulfides by a Michael reaction. Lima et al.[109] have used this process with hydroxyethyl acrylate in forming telechelic polymers and report on the efficiency and limitations of the process.

Various functional RAFT agents used to provide end functional polymers are listed in Tables 1–6. These allow the syntheses of polymers with carboxylic acid,[12,31] hydroxyl,[109] and primary amine (via phthalimido end groups)[12,30] and other end groups.

Bipyridine (**101**; Scheme 12)[193] and terpyridine (**102**) functional dithioesters[194] have been used in RAFT polymerization and thence to form ruthenium complexes. The RAFT-synthesized polymer formed with **102** was used to make ruthenium connected polystyrene-(Ru^{II})-PNIPAM blocks.

Chen et al.[195,196] have shown that it is possible to form new functional RAFT agents by single monomer insertion using the RAFT process. The process was used to synthesize the necessary RAFT agents for producing polymers with anthracene groups[195] or acenaphthalene[196] at the chain ends. The extent of propagation was controlled by choice of the monomer and RAFT agent concentrations and may be aided by penultimate unit effects (a first monomer addition is typically substantially faster than subsequent monomer additions).

RAFT homopolymerization of MAH results in insertion of a single MAH unit simply because the monomer has a low propensity for propagation.[197,198] This process may be used to place a MAH unit at the end of a RAFT synthesized polymer chain to create a functional macroRAFT agents.[197,198]

This single-monomer unit insertion processes have some parallel with the very early work of Zard and co-workers who described a RAFT process for synthesizing adducts of xanthates to electron-deficient monomers (e.g. *N*-methylmaleimide).[199]

Gradient Copolymers

It should be noted that, due to the effects of compositional drift, most copolymers prepared by RAFT polymerization fall under the description gradient copolymers.[12] Examples of gradient copolymers include a wide range of hydrophilic-hydrophobic copolymers based on long chain acrylates (e.g. octadecyl acrylate; ODA).[113,114] These copolymers include poly(ODA-*grad*-NVP) and poly(ODA-*grad*-MAH) prepared with trithiocarbonate **64**[114] and which find use as dispersants in polypropylene–clay nanocomposites. Other examples are the terpolymer of styrene, MAH, and NVP[200] and various copolymers based on phosphonated monomers.[201]

A detailed study of the kinetics of RAFT copolymerization of styrene and MMA with dithioacetate RAFT agents has been reported.[34] Transfer constants ($C_{\mathrm{tr}} = k_{\mathrm{tr}}/k_{\mathrm{p}}$, where $k_{\mathrm{tr}} = k_{\mathrm{add}}[k_{\beta}/(k_{-\mathrm{add}} + k_{-\beta})]$; see Scheme 1) at 40°C were reported for the PMMA and polystyrene macroRAFT agents in polymerizations of MMA, styrene, and the azeotropic copolymerization of MMA and styrene (Table 9). The data indicate that in styrene polymerization, 50% conversion of the PMMA macroRAFT agent is achieved at very low monomer conversion (~0.16%), while, in MMA polymerization, the polystyrene macroRAFT agent is half consumed at a much higher conversion (~57%). The results provide further quantitative support the observation that when preparing block copolymers of methacrylates with styrene (and other monosubstituted monomers) it is best to prepare the methacrylate block first.

The results also further understanding of the observation that copolymerizations of monomers may be controlled even though homopolymerization of the same monomer may be uncontrolled or poorly controlled by particular RAFT agents.[4] Other examples of this phenomena are copolymerizations of the captodative monomer ethyl α-acetoxyacrylate (EAA) with acrylic monomers (BA, AA, DMA, DMAEA) with the xanthate RAFT agent **70**[120] (EAA homopolymerization is not controlled with **70**), and the above-mentioned copolymerizations of ODA and other acrylic monomers with MAH or NVP with trithiocarbonate RAFT agent **64** (MAH does not readily homopolymerize, NVP homopolymerization is not controlled with trithiocarbonates).[114]

Table 9. Transfer constants for dithioacetate macroRAFT agents at 40°C[34]

	Monomer(s)		
MacroRAFT	S	MMA	S/MMA[A]
PS	220	0.83	75
PMMA	420	40	155

[A] Random copolymer, [S]:[MMA] ratio 0.53 (azeotropic composition). Values based on penultimate model.

Block Copolymers

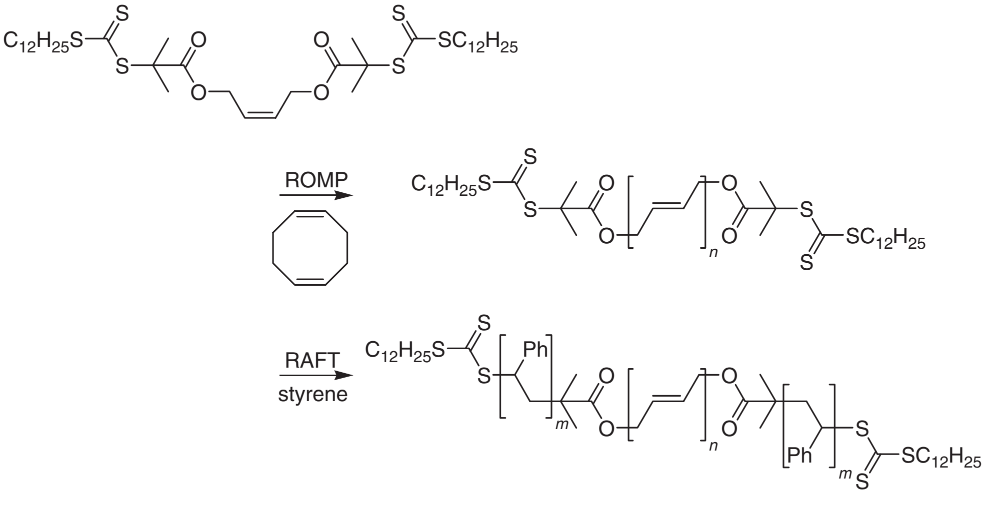
Several approaches to polyolefin block copolymers which make use of RAFT polymerization have been reported. A synthesis of polyethylene with terminal *t*-butyl trithiocarbonate, dithiobenzoate or *N*,*N*-diethyldithiocarbamate groups as potential RAFT agents has been reported.[202] It should be noted that RAFT agents with R = primary alkyl would not usually be anticipated to be effective because primary alkyl radicals are poor homolytic leaving groups.

Telechelic polybutadienes bearing trithiocarbonate end groups were prepared by ring-opening metathesis polymerization (ROMP) of cyclooctadiene and subsequently used to make ABA triblocks by RAFT polymerization of styrene (Scheme 13) or *t*-butyl acrylate.[203]

The synthesis[125] and use[126] of dithiocarbamate RAFT agents containing blocks derived from liquid Kraton (a monohydroxy end-functional poly(ethene-*co*-butene)) has been described. A bis-RAFT agent (analogous to **86**) was used to prepare poly(ethene-*co*-butene)-*block*-PBA-*block*-poly(ethene-*co*-butene).[126] A range of hydrophilic–hydrophobic block copolymers based on long chain acrylates (ODA) have been reported.[113,204] PODA is compatible with polypropylene.

RAFT polymerization of styrene with trithiocarbonate **103** (Scheme 14, with protected diol functionality in the 'R' group) was used to form a precursor from which cationic ring opening polymerization of 1,3-dioxepane was initiated.[205]

Polylactide-*block*-PDMA-*block*-polystyrene[206] and PEO-*block*-PMMA-*block*-polystyrene[58] were prepared



Scheme 13.

from the appropriate hydroxy end-functional polymer by end-functionalizing that polymer as a RAFT agent (**104** or **105** respectively; Scheme 15) and sequential RAFT polymerization.

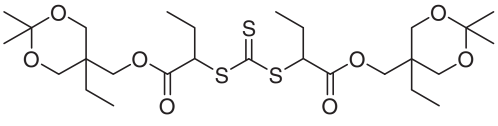
Other examples of block copolymers are acrylamide-based block copolymers,[105] PAN-*block*-PMA,[207] poly-(styrene-*co*-AN) (SAN) block copolymers from methacrylate (DMAEMA, GMA, MMA) or poly(styrene-*co*-MAH) macro-RAFT agents (note that SAN and SAN block copolymers by RAFT have been reported previously[4]),[68] and PBMA-*block*-PDMAEMA-*block*-PBMA and PDMAEMA-*block*-PBMA-*block*-PDMAEMA,[208] hydrophilic–hydrophobic block copolymers (including PBA-*block*-PDMA, PBA-*block*-PNAP, PBA-*block*-poly(2-(methylsulfinyl)ethyl acrylate)).[72,209,210] Further examples with specific applications are mentioned in the other sections of this review.

Multiblock copolymers can be prepared from polymers containing trithiocarbonate linkages.[197,211] One method of synthesizing these involves a ring opening RAFT polymerization making use of the cyclic trithiocarbonate **106** (Scheme 16).[211] Multiblock copolymers have also been prepared from the multi-dithiocarbamate **107**.[126]

Star Polymers

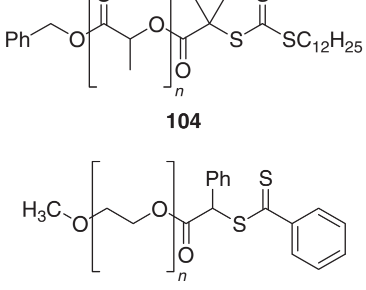
A strategy for kinetic simulation of star formation by RAFT polymerization making use of multi-RAFT agents has been developed.[212]

Star-block copolymers with a hexa(dithiobenzoate)-functionalized ruthenium tris(bipyridine)[213] as core and di-[214] or tri-block arms[215] have been reported. Synthesis of stars with triblock arms based on acenapthalene, the coumarin derivative **108** (Scheme 17), and NIPAM provided light-harvesting systems with an energy gradient from the periphery to the core.[215]



103

Scheme 14.



104

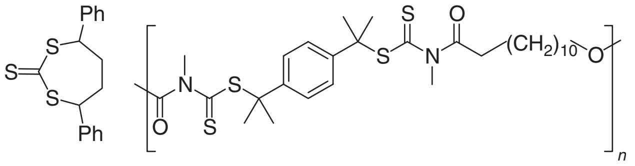
105

Scheme 15.

Dendrimer cores (16 dithiobenzoate) were synthesized and used to make *star*-polystyrene and *star*-(polystyrene-*block*-PMA).[216] Second or third generation polyethyleneimine dendrimers were used to prepare cores with eight or sixteen dithiobenzoate ends **109** (Scheme 18) for synthesis of *star*-polystyrene and *star*-(polystyrene-*block*-PMA)[217] or *star*-PNIPAM.[218]

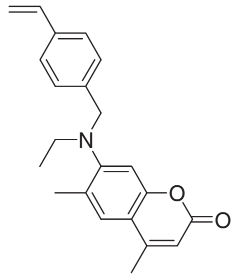
First, second, and third generation (three, six, and twelve arm) dendrimers functionalized with benzyl trithiocarbonate groups **110** were used to make *star*-polystyrene, *star*-PBA, *star*-(PBA-*block*-polystyrene), and *star*-(polystyrene-*block*-PBA).[219] Hyperbranched polyglycerol (functionality ~16) also functionalized as benzyl trithiocarbonate groups **110** was used to make *star*-PEA.[220]

A tris-trithiocarbonate RAFT agent with a thiourethane-isocyanurate core **111** (Scheme 19) was used to synthesize a three-armed *star*-polystyrene.[118]



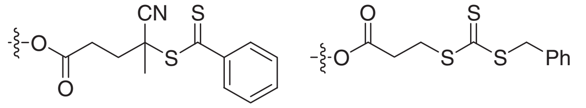
106 S BA **107**

Scheme 16.



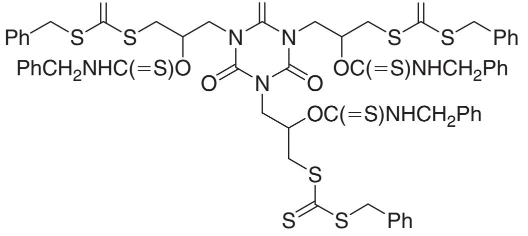
108

Scheme 17.



109 **110**

Scheme 18.



111

Scheme 19.

Microgels and Nanoparticles

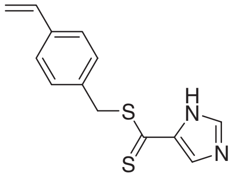
In this section we consider direct formation of polymer microgels or nanoparticles in a solution polymerization process or by self-assembly and crosslinking of block copolymers. Surface functionalization of nanoparticles by RAFT polymerization is considered in the next section. Formation of particles and nanoparticles by heterogeneous polymerization (emulsion, miniemulsion polymerization) is discussed above.

The three basic processes for forming nanoparticles described in the previous review[4] will be distinguished.

(a) (Co)polymerization of a di- (or higher) functional monomer to form a crosslinked core. There are two ways of adapting this process to form a star-microgel. The so-called 'arm-first' process for star synthesis involves synthesis of a macroRAFT agent which is then used in RAFT (co)polymerization of a multifunctional monomer. The second approach relies on the RAFT agent functionality that is retained in the crosslinked core to enable arms to be grown from the core is a subsequent RAFT polymerization step. The two approaches may be combined to synthesize mikto-arm stars. Recent examples are the preparation of stable microgels by copolymerization of divinylbenzene and 4VP[221] or of AA and ethylene glycol diacrylate[222] in the presence of polystyrene dithiobenzoate or by copolymerization of AA or AM and *N*,*N*′-methylenebisacrylamide in the presence of an *O*-ethyl xanthate.[223]

(b) Hydrophilic–hydrophobic (or solvophilic–solvophobic) block copolymers are self-assembled to form micelles (or other supramolecular structures). A crosslinking reaction is then used to stitch together the core, shell and/or mid-block sections to form a stable structure. Again it is possible to perform a subsequent RAFT polymerization making use of retained RAFT agent functionality step to elaborate the structure. Recent examples are crosslinked micelles with a PNIPAM core produced from PNIPAM-*block*-PHEA or PNIPAM-*block*-polystyrene (cross linking with *N*,*N*′-methylenebisacrylamide)[224] and shell-crosslinked structures from poly(styrene-*alt*-MAH)-*block*-polystyrene,[225] or PEO-*block*-P(DMA-*co*-NAS)-*block*-PNIPAM.[226] Shell-crosslinked micelles have also been produced from RAFT-synthesized block copolymers self-assembled on gold nanoparticles.[227]

(c) Self-condensing vinyl polymerization involves (co)polymerization of a monomer that also contains RAFT agent functionality. A recent example is hyperbranched PNIPAM prepared by copolymerization of NIPAM with **112** (Scheme 20)[93,228] and used in protein separation.[228]


112

Scheme 20.

There have also been further studies on network formation by RAFT polymerization.[208]

Polymer Brushes, Graft Copolymers, Comb Polymers, and Surface Modification

Grafting-From Processes

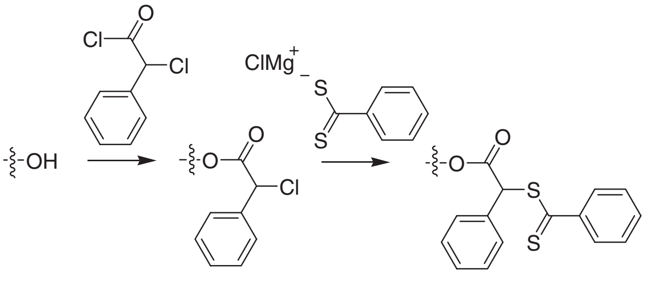
Two basic approaches are used. The first involves surface modification to attach RAFT agent functionality and RAFT polymerization as a subsequent step. The second involves forming radicals on the surface (e.g. by irradiation or from attached initiator functionality) to initiate polymerization in the presence of a 'free' RAFT agent which becomes attached to the surface as a consequence of RAFT polymerization.

Further papers have been published on grafting to hydroxy-functional materials, for example, cellulose (e.g. cotton fabric or paper functionalized as shown in Scheme 21),[229,230] PVA (**113**, **114**; Scheme 22).[231]

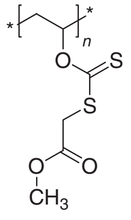
Functionalized multi-walled carbon nanotubes were prepared by derivatization of surface carboxy groups as dithiobenzoates (Scheme 23).[232] RAFT polymerization gave PHPMAM grafts.

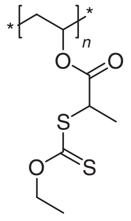
Polystyrene–clay nanocomposites were prepared by RAFT polymerization in the presence of clay intercalated with the alkyl ammonium dithiobenzoate **17**.[85]

Polymerizations initiated from silica particles have been reviewed.[233] Surface modification of silica particles with silane functional RAFT agent **18** was used to attach dithiobenzoate groups which were subsequently grafted with polystyrene, PBA or PBA-*block*-polystyrene by RAFT polymerization.[86] Dithiobenzoate RAFT agents with tertiary 'R' were attached by reacting amino functional silica



Scheme 21.


113


114

Scheme 22.

particles with **37**.[95] These were then used to form PMMA brushes.

Porous silica particles surface were modified by immobilization of 2,2-azobis(2-cyanopentanoic acid) and grafted with MAA-EGDMA by RAFT polymerization with cumyl dithiobenzoate in the presence of L-phenylalanine anilide to leave a crosslinked molecularly imprinted film which was used as a chromatographic support.[234]

Pirri et al.[235] have described a new method for forming PDMA or a poly(DMA-*block*-GMA) brushes on glass or silica surfaces by RAFT polymerization. A glass microscope slide surface was derivatized with a thiol-functional organosilane, (3-mercaptopropyl)trimethoxysilane. The slide was then immersed in a *N,N*-dimethylformamide solution of monomer (DMA), initiator (AIBN), and RAFT agent **8** and heated to 60°C for 48 h. A similar process was applied to graft from silica beads.[235] These materials were then used to bind oligonucleotide molecules.

The above-mentioned processes are 'away from' processes where the 'R' is bound to the substrate. 'Attached to' processes where 'Z' is bound to the substrate have also been described. Merrifield resin and silica particle supported RAFT agents have been synthesized by sequential treatment of chloromethylphenyl functionality with sodium methoxide and elemental sulfur and methyl-α-bromophenylacetate (Scheme 24).[236]

A PHEMA brush was formed on a poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film by first carrying out surface modification with an oxygen plasma to introduce peroxide functionality. This functionality was used to initiate RAFT polymerization of HEMA in the presence of cumyl dithiobenzoate to produce FEP-*graft*-(PHEMA).[237]

A PVDF surface was first chemically modified, to introduce hydroxyl groups. These were then esterified with 2,2-azobis(2-cyanopentanoic acid) and this functionality used to initiate RAFT polymerization of MMA, or PEGMA in the presence of cumyl dithiobenzoate. PVDF-*graft*-(PMMA-*block*-PDMAEMA) and PVDF-*graft*-(PPGEMA-*block*-PDMAEMA) were prepared.[238]

Other papers cover RAFT polymerization of AA/**65** from a PVDF surface previously irradiated with an electron beam[115] and graft copolymerization from a PP surface was achieved by gamma-irradiation of a solution of styrene and 1-(2-isocyanatopropan-2-yl)-3-(propen-2-yl)benzene and **38** in the presence of a PP 'lantern'.[239]

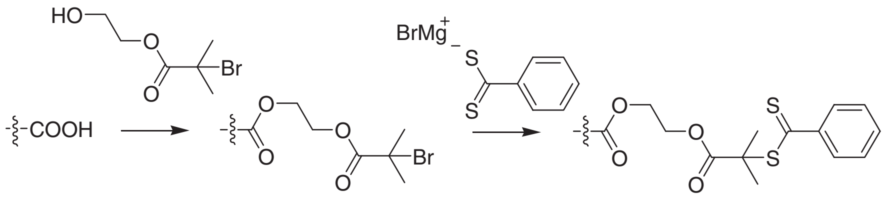
Several papers report the use of RAFT polymerization to prepare a backbone polymers/macroinitiator for comb polymer synthesis. Poly(*N*-phenyl maleimide-*co*-(4-chloromethylstyrene)) was prepared by RAFT copolymerization with **7** and used as a macroinitiator for ATRP of styrene (CuCl/2,2′-bipyridine catalyst) to form poly(*N*-phenyl maleimide-*co*-4-chloromethylstyrene)-*comb*-polystyrene.[61] Similarly poly(styrene-*co*-(vinylbenzenesulphonyl chloride)) prepared by RAFT copolymerization with **7** was used as a macroinitiator for ATRP of MMA (CuCl/2,2′-bipyridine catalyst).[62] Poly(styrene-*co*-(4-chloromethylstyrene))-*block*-PMA was used as a macroinitiator for cationic ring-opening polymerization of tetrahydrofuran ($AgClO_4$ catalyst).[240]

Processes based on the use of dithiocarbamate photoiniferters need not involve RAFT. They are mentioned here because they involve the use of similar reagents and similar strategies for attachment of the thiocarbonylthio functionality. Recent reports include dithiocarbamate photoiniferter based grafting of MMA to silicon substrates,[241] and the grafting of acrylates (PEGA, TFEA) to polymer surfaces prepared by thiol-ene polymerization[242,243] in the preparation of microfluidic devices[243] and other applications.

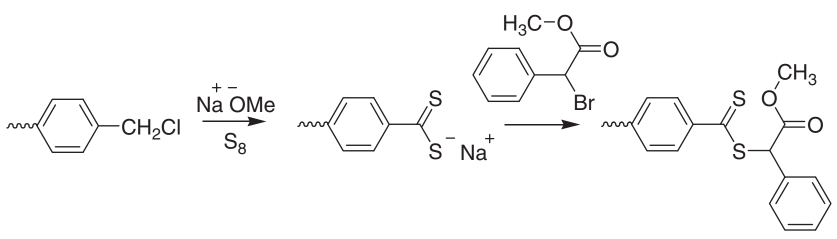
Grafting-To Processes

Dithioesters and trithiocarbonates can act as anchoring groups for use in a *grafting-to* approach. The RAFT agents (benzyl dithiobenzoate **20** and dibenzyl trithiocarbonate **52**) and derived RAFT-synthesized polystyrenes were shown to bind to form monolayers on gold surfaces without prior transformation of these thiocarbonylthio groups to thiols.[244]

Copolymers of *N*-(meth)acryloyl succinimide or pentafluorophenyl methacrylate (these monomers, NAS, NMS, and



Scheme 23.



Scheme 24.

PFMA are referred to as active esters of (meth)acrylates) have been produced by RAFT polymerization and served as substrates for biofunctionalization or other grafting reactions using *grafting-to* processes.[66,73,245,246] Recent examples include poly(*t*-butyl acrylamide-*block*-poly(*N*-acryloylmorpholine-*co*-NAS)[245] poly(DMA-*co*-NAS),[246] PFMA-*block*-PNAM,[73] and PFMA-*block*-PMMA.[73]

Grafting-Through Processes

Clay nanocomposites formed by RAFT polymerization with the use of intercalants containing monomer functionality.[247] A RAFT-synthesized glycopolymer was grafted to silica particles by copolymerization of silica particles modified with 3-(trimethoxysilyl)propyl methacrylate (TPSM).[181]

PBA and PDMA grafts have been formed on poly(divinylbenzene) microspheres.[248] The process involved RAFT polymerization of the monomer in the presence of microspheres prepared by precipitation polymerization and which possess pendant double bonds. Cumyl dithiobenzoate **9** was used as RAFT agent.

Other Approaches

A PNIPAM-*block*-PTPSM was prepared by RAFT polymerization. This block copolymer self-assembles into micelles with PTPSM at the core and PNIPAM as a shell. A base-catalyzed sol–gel process within the PTPSM core resulted in PNIPAM-encapsulated silica nanoparticles.[249]

Supramolecular Structures

Stimuli responsive polymers and self-assembled structures have attracted significant interest. Self assembly is an integral step in the process of particle formation during emulsion polymerization using amphiphilic RAFT agents and many of the processes for forming nanoparticles and surfaces mentioned above and in the previous review.[4] The tolerance of RAFT polymerization to a wide variety of polar and protic monomers means that it is one of the most versatile for forming amphiphilic polymers.

The work of the McCormick group in designing block copolymers that contain segments that respond to changes in pH, temperature, or ionic strength has been reviewed.[13] Thermally responsive systems based on the use of polymers containing PNIPAM blocks[72,102,104,105,111,112,226,228,249–252] have been reported by many groups. Polymers with PNAPM blocks have been reported in a similar context.[88]

Honeycomb-structured, porous films formed as breath figures with pore sizes ranging from 200 nm to 7 μm have been prepared from RAFT-synthesized polymers and the dependence on polymer composition, molecular weight, and architecture has been reviewed.[14] A more general review on the formation and applications of honeycomb polymers by the breath figure approach has also been published.[253] Recent reports include honeycomb structures formed by assembly of polypyrrole-containing block copolymers[254] and comb polymers formed by grafting polystyrene from cellulose.[255] The former have been suggested as scaffolds for cell growth.[254]

Summary

The period since the publication of our last review has seen the publication of more than 200 papers on various aspects of RAFT polymerization. A change in focus from the study of the scope and mechanism of RAFT polymerization towards applications of the process is clearly evident.

Acknowledgments

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RESEARCH FRONT

Review

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Living Radical Polymerization by the RAFT Process – A Second Update

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This paper provides a second update to the review of reversible deactivation radical polymerization achieved with thiocarbonylthio compounds (ZC(=S)SR) by a mechanism of reversible addition–fragmentation chain transfer (RAFT) that was published in June 2005 (*Aust. J. Chem.* **2005**, *58*, 379–410). The first update was published in November 2006 (*Aust. J. Chem.* **2006**, *59*, 669–692). This review cites over 500 papers that appeared during the period mid-2006 to mid-2009 covering various aspects of RAFT polymerization ranging from reagent synthesis and properties, kinetics and mechanism of polymerization, novel polymer syntheses and a diverse range of applications. Significant developments have occurred, particularly in the areas of novel RAFT agents, techniques for end-group removal and transformation, the production of micro/nanoparticles and modified surfaces, and biopolymer conjugates both for therapeutic and diagnostic applications.

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Introduction

Radical polymerization is one of the most widely used processes for the commercial production of high-molecular-weight polymers.[1] The emergence of techniques for implementing reversible deactivation radical polymerization (RDRP), which serve to impart living characteristics to the process, has provided a new set of tools for polymer chemists that allow control over the polymerization process while retaining much of the versatility of conventional radical polymerization. It is no longer a formidable task to apply radical polymerization to the synthesis of blocks, stars, or other polymers of complex architecture. New materials with the potential of revolutionizing a large part of the polymer industry continue to appear. The polymerization techniques that are receiving greatest attention are nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT).

There remains some controversy over the use of the terms 'living' and 'controlled' in describing processes for radical polymerizations such as ATRP, NMP, or RAFT.[2] The recommendation of the International Union of Pure and Applied Chemistry (IUPAC), that a living polymerization is 'a chain polymerization from which irreversible chain transfer and irreversible

Graeme Moad obtained his B.Sc. (Hons) and Ph.D. from the Adelaide University in the field of organic free radical chemistry. After undertaking post-doctoral research at Pennsylvania State University in the field of biological organic chemistry he joined CSIRO in 1979 and is currently a chief research scientist and a research team leader. Dr Moad is author or co-author of 147 papers in refereed journals, co-inventor of 32 patent families (eight relate to the RAFT process) and co-author of the book 'The Chemistry of Radical Polymerization'. His papers have been cited more than 9000 times and his h-index is 46. His research interests lie in the fields of polymer design and synthesis (radical polymerization, reactive extrusion, polymer nanocomposites) and polymerization kinetics and mechanism.

Ezio Rizzardo is a graduate of the University of New South Wales and he received his Ph.D. from the University of Sydney for his studies on the photochemistry of organic nitro compounds. He joined CSIRO in 1976 after postdoctoral research on the synthesis of biologically active organic compounds at Rice University, RIMAC, and the Australian National University. His CSIRO research has focussed on developing methods for controlling free radical polymerization. For this he has received a number of awards including the RACI Australian Polymer Medal and the CSIRO Chairman's Gold Medal. Ezio is a CSIRO Fellow and a Fellow of the Australian Academy of Science.

San H. Thang completed his B.Sc. (Hons) in 1983 and Ph.D. in 1987 both from Griffith University. He joined CSIRO in 1986 as a Research Fellow, and then moved to ICI Australia Research Group in December 1987 to undertake the challenge of industrial research. He returned to CSIRO in late 1990 and currently is a Senior Principal Research Scientist at Molecular and Health Technologies where his research focuses primarily on the interface between organic and polymer chemistry. San is a leading expert in the field of free radical chemistry and polymer chemistry. He is a co-inventor of the living radical polymerization by reversible addition–fragmentation chain transfer (RAFT process).

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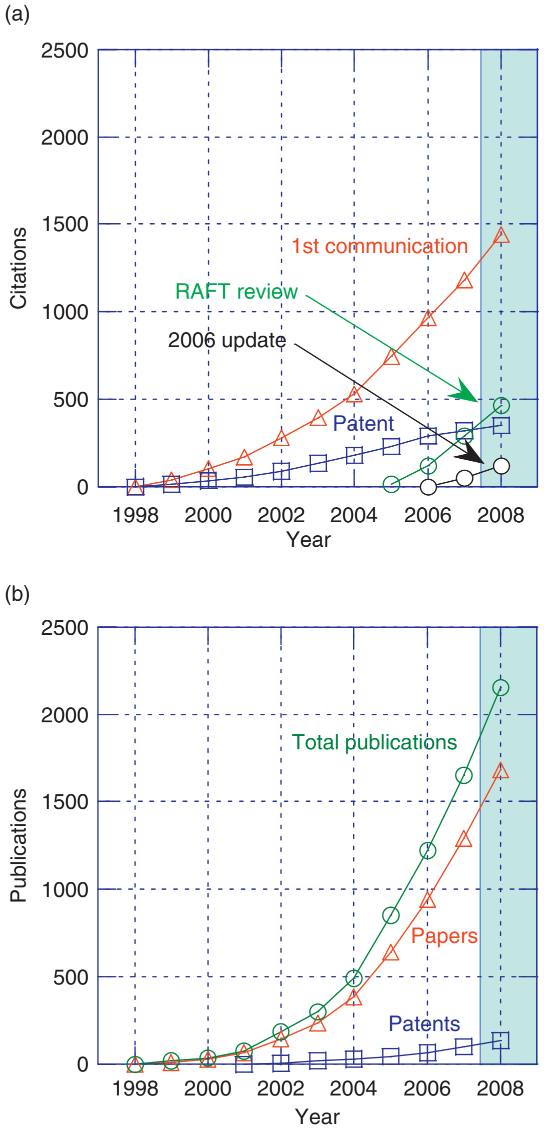


Fig. 1. (a) Cumulative citations for our first communication on RAFT (△),[5] our first patent (□)[6] and our 2005 (◯)[7] review on RAFT polymerization and its 1st update (◯).[8] Based on a SciFinder search carried out in March 2009. (b) Total publications, papers, and patents on RAFT polymerization based on SciFinder search of terms 'RAFT Polymerization', 'Reversible Addition Fragmentation Transfer' & 'radical', 'MADIX' & 'radical'. The term 'papers' includes journal, articles, communications, letters and reviews but does not include conference abstracts.

chain termination (deactivation) are absent', precludes use of the adjective 'living' in referring to these processes.[3] 'Controlled', when used by itself, is also contrary to IUPAC recommendations. It is incorrect to use 'controlled' in an exclusive sense to indicate a particular form of polymerization because the word has an established, much broader, usage. Use of the terms 'controlled living', 'controlled/living', 'pseudo-living', and 'quasi-living' is also discouraged. An IUPAC task group has recently recommended the term reversible deactivation radical polymerization (RDRP) to describe polymerizations, such as ATRP, NMP, or RAFT, that entail equilibria between active and dormant chains.[4] This term is not intended to have any connotations as to the fraction of living chains that might be present in a particular polymerization process.

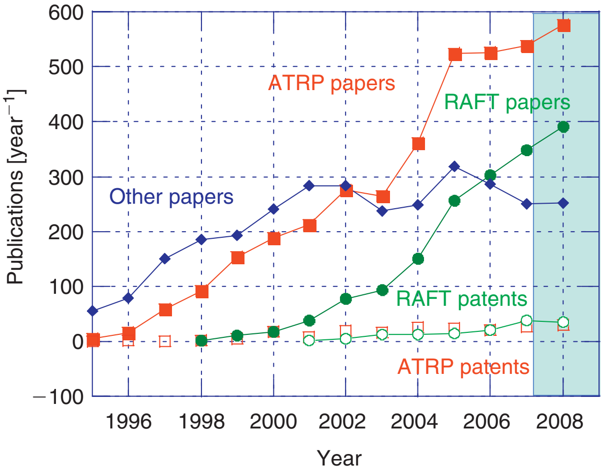
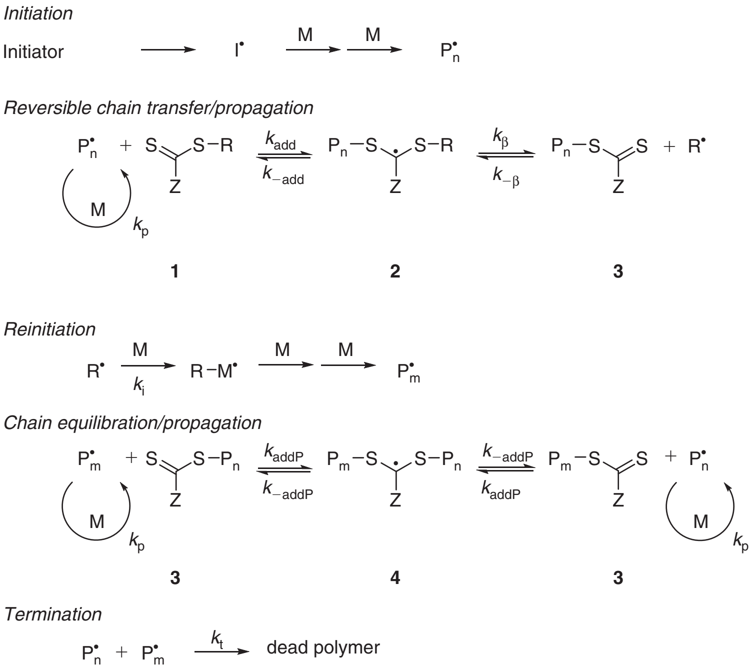


Fig. 2. Publications per year on reversible deactivation radical polymerization (RDRP) based on a SciFinder search in March 2009 of terms for RAFT (●) ('RAFT Polymerization', 'Reversible Addition Fragmentation Transfer', 'MADIX polymerization'), for ATRP (■) ('ATRP polymerization' and 'atom transfer radical polymerization') and for other (◆) ('living radical polymerization', 'controlled radical polymerization' less those counted under RAFT or ATRP). 'Papers' (closed symbols) includes journal articles, reviews and letters but not conference abstracts. 'Patents' (open symbols) refers to patent families.

It remains acceptable to use the term 'living radical polymerization' to describe a hypothetical process in which termination is indeed absent. It is in this context that we use 'living radical polymerization' in the title of this review and the previous articles of this series. We do not intend to imply that termination is absent from any polymerizations described herein. Many systems do display the observable characteristics normally associated with living polymerizations and in a few cases, termination, while undeniably present, is undetectable using current techniques.

The increasing importance of RAFT is illustrated by Fig. 1, which shows the cumulative citations for our first communication on RAFT with thiocarbonylthio compounds,[5] the first RAFT patent,[6] and the previous reviews in the *Australian Journal of Chemistry*.[7,8] It should be noted that not all papers on RAFT polymerization cite these sources, nor are all of the papers citing these documents directly relevant to RAFT polymerization. Fig. 2 shows that the remarkable growth in publication of papers covering all forms of RDRP has continued unabated. The total number of papers that mention 'RAFT polymerization' has more than doubled over the period 2006–2009 with more than 1000 papers being published, and approximately one-third of papers on RDRP now pertain to the concept 'RAFT polymerization'.

This review is primarily intended to cover the literature on RAFT polymerization that has appeared since publication of the update review published in the *Australian Journal of Chemistry* in late 2006.[8] We also refer to some earlier papers that were not included in that or the earlier reviews. Work cited in the previous reviews[7,8] is only mentioned again where necessary to put the more recent work in context. The past 2 years has seen the publication of further general reviews detailing the RAFT process which include works by Moad, Rizzardo, and Thang,[9–12] a *Handbook of RAFT Polymerization*,[13] and a highlight article by Barner-Kowollik and Perrier[14] on the future of RAFT. Reviews on specific areas include the kinetics and



Scheme 1. Mechanism of RAFT polymerization.

mechanism of RAFT polymerization,[15–18] the use of RAFT to probe the kinetics of radical polymerization,[19,20] the use of RAFT in organic synthesis,[21] amphiphilic block copolymer synthesis,[22,23] the synthesis of end functional polymers,[24] the synthesis of star polymers and other complex architectures,[25,26] the use of trithiocarbonate RAFT agents,[27] the use of xanthate RAFT agents (MADIX),[28] polymerization in heterogeneous media,[29–32] RAFT polymerization initiated with ionizing radiation,[33] polymer synthesis in aqueous solution,[34–37] surface and particle modification,[38,39] synthesis of self assembling and/or stimuli responsive polymers,[36,40] RAFT-synthesized polymers in drug delivery,[22,41] and other applications of RAFT-synthesized polymers.[30,42,43] The process is also given substantial coverage in most recent reviews that, in part, relate to polymer synthesis, living or controlled polymerization, or novel architectures. Some of these documents are referred to in subsequent sections of this review.

Mechanism of RAFT

The key feature of the mechanism of RAFT polymerization with thiocarbonylthio compounds, as proposed in our first communication on the subject,[5] is the sequence of addition–fragmentation equilibria shown in Scheme 1. Initiation and radical–radical termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical ($P_n^\bullet$) to the thiocarbonylthio compound [RSC(Z)=S (**1**)] followed by fragmentation of the intermediate radical provides a polymeric thiocarbonylthio compound [P_nS(Z)C=S (**3**)] and a new radical (R$^\bullet$). Reaction of this radical (R$^\bullet$) with monomer forms a new propagating radical ($P_m^\bullet$). Rapid equilibrium between the active propagating radicals ($P_n^\bullet$ and $P_m^\bullet$) and the dormant polymeric thiocarbonylthio compounds (**3**) provides equal probability for all chains to grow and allows for the production of narrow dispersity polymers. When the polymerization is complete (or stopped), most of the chains retain the thiocarbonylthio end-group and can be isolated as stable materials.

The reactions associated with RAFT equilibria shown in Scheme 1 are in addition to those (i.e., initiation, propagation, transfer, and termination) that occur during conventional radical polymerization. In an ideal RAFT process, the RAFT agent should behave as an ideal transfer agent. Thus, as with radical polymerization with conventional chain transfer, the kinetics of polymerization should not be directly affected by the presence of the RAFT agent beyond those affects attributable to the differing molecular weights of the reacting species. Radical–radical termination is not directly suppressed by the RAFT process. Living characteristics are imparted when the molecular weight of the polymer formed is substantially lower than that which would be formed under the same conditions but in the absence of a RAFT agent, and is such that the number of polymer molecules with RAFT agent-derived ends far exceeds the number formed as a consequence of termination. Many RAFT polymerizations stray from this ideal. Although the basic mechanism shown in Scheme 1 is generally not disputed, much debate continues on the detailed kinetics of the RAFT process, the rapidity with which the various equilibria are established, and what side reactions might occur to complicate the process in specific circumstances.

Mechanisms for retardation in RAFT polymerization mediated by, in particular, dithiobenzoate RAFT agents continue to attract significant interest. Mass spectrometry has been used to provide evidence to support the occurrence of intermediate radical termination during RAFT polymerization of acrylates,[44] styrene (St),[45,46] and *N*-acryloylmorpholine (NAM)[47] with dithiobenzoate RAFT agents. A recent paper[48] purports to suggest a possible compromise between the 'slow fragmentation' and 'intermediate radical termination' models for retardation in RAFT polymerization with dithiobenzoate RAFT agents. According to the proposed model intermediate radical termination occurs, but only for initiator-derived or oligomeric species (chain length <2).[48,49]

Further details of the so-called 'missing reaction step' mechanism for retardation in RAFT polymerization with dithiobenzoate RAFT agents have also been published.[50] Some support for this mechanism comes from studies on 2,2′-azoisobutyronitrile-α-^{13}C-initiated polymerization of St.[51]

Kinetic analysis together with Monte Carlo simulation of the reaction of alkoxyamines with dithiobenzoates (**22**, **49**) was investigated as a means of estimating rate constants for addition and fragmentation.[52] However, side reactions proved to be an issue when applying the method.

The initialization process (consumption of the initial RAFT agent) in RAFT (co)polymerization has been studied by ^{1}H NMR spectroscopy for St/maleic anhydride (St/MAH) with RAFT agents **22** and **24**,[53] methyl acrylate (MA) with RAFT agents **22**, **24**, and **92**,[54] and of vinyl acetate (VAc) and *N*-vinylpyrrolidone (NVP) with xanthates **207**, **209**, and **211**.[55] For many of these systems so-called selective initialization was observed in which there is substantial conversion of the initial RAFT agent into a single unit species before conversion into higher molecular weight chains. The effect is attributed to the rate constant of addition of the 'R' radical to MA being substantially slower than that for propagation.[56] The course of the RAFT polymerization of butyl acrylate (BA) and St with cumyl (**22**) and cyanoisopropyl dithiobenzoate (**24**) was followed by electron spin resonance (ESR) spectroscopy.[57] ^{13}C NMR spectroscopy was used to follow the initiation of St polymerization with AIBN-α-^{13}C and with cumyl (**22**) and cyanoisopropyl (**24**) and benzyl dithiobenzoates (**61**) and with cyanoisopropyl dodecyl trithiocarbonate (**121**).[51] An unexpected finding was the observation of ^{13}C chemically induced nuclear polarization (CIDNP) for the ketenimine formed by cage recombination of the AIBN-derived cyanoisopropyl radicals. Selective initialization was observed for the more active RAFT agents **22**, **24**, and **121** (with good 'R' leaving group). However, with benzyl dithiobenzoate (**61**) (poor 'R' leaving group relative to propagating species), consumption of the initial RAFT agent is slow with respect to the rate of polymerization and higher molecular weight species are formed from the inception of RAFT polymerization.

The rate constant for chain transfer (k_{tr}) for a RAFT agent is given by the expression in Eqn 1 and depends on the rate of addition of the propagating radical to the RAFT agent and a coefficient (ϕ) which describes how the intermediate radical (**2**) partitions between starting materials and products – refer to Scheme 1:

$$k_{tr} = k_{add}\phi = k_{add}\left[\frac{k_{\beta}}{k_{-add} + k_{\beta}}\right] \tag{1}$$

The transfer agent-derived radical (R$^{\bullet}$) is also partitioned between adding to monomer and reacting with the macro-RAFT agent (**3**). We, therefore, define a rate constant associated with this reaction (k_{-tr}) as shown in Eqn 2.

$$k_{-tr} = k_{-\beta}\phi_{\beta} = k_{-\beta}\left[\frac{k_{-add}}{k_{-add} + k_{\beta}}\right] \tag{2}$$

Knowledge of the partition coefficients ϕ and ϕ_{β} (note $\phi_{\beta} = 1 - \phi$) and C_{-tr} is required for an understanding of RAFT agent activity. The high reactivity of RAFT agents is such that C_{-tr} is seldom zero. Transfer constants measured by methods which include an assumption that C_{-tr} is zero or that k_{β} is zero will typically underestimate the actual C_{tr}. These values should be called apparent transfer constants C_{tr}^{app}. In some cases, values of C_{tr} may be higher than C_{tr}^{app} by several orders of magnitude.[56] An indication that the reverse reaction is important is the dependence of C_{tr}^{app} on the RAFT agent concentration and on monomer conversion.[56,58,59] The spread in literature values for C_{tr}^{app} may be attributed to this effect. Note that the situation is simplified for the case of macro-RAFT agents in homopolymerization where, notwithstanding effects of chain length, the forward and reverse reactions are the same ($C_{tr} = C_{-tr}$) and the partition coefficient ϕ is 0.5.

For less active RAFT agents ($C_{tr} \leq 1$), transfer constants for RAFT agents may be determined using the usual methods (e.g., the Mayo method) with little loss of accuracy. Experimental values of kinetic parameters associated with the RAFT process (addition rate constants (k_{add}), fragmentation (k_{β}, k_{-add}) rate constants, and forward ($C_{tr} = k_{tr}/k_{p}$), reverse ($C_{-tr} = k_{-tr}/k_{i}$) and apparent transfer constants (C_{tr}^{app})) in the literature through 2006 were summarized by Moad et al.[9] Data for C_{tr}^{app}, C_{tr}, and C_{-tr} that has appeared since that review are summarized in Table 1. A new method of estimating $k^{*} = 1/C_{tr}^{app}$ based on fitting oligomer molecular weight distributions was recently reported.[60]

Instrumentation and reactor design to allow direct online monitoring of the RAFT polymerization by viscometry, ultraviolet-visible spectrophotometry (with a photodiode array detector), refractive index, and multi-angle light scattering has been described and applied to study the time/conversion dependence of molecular weight for the polymerization of BA with RAFT agent **154** as a function of the RAFT agent concentration.[61]

The effect of the monomer feed composition on C_{tr}^{app} for RAFT agents in butyl acrylate (BA)/St and methyl methacrylate (MMA)/BA copolymerization has also been studied.[62] It was proposed that effective transfer constants in copolymerization $\langle C_{tr} \rangle$ might be estimated on the basis of the reactivity ratios and the homo ($C_{tr,nn}$) and cross transfer constants ($C_{tr,nm}$).

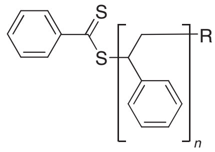
RAFT-Related Processes

Polymerization of VAc and similar monomers mediated by organocobalt porphyrin complexes is proposed to involve a RAFT-like mechanism called associative degenerative chain transfer.[74–76] A reversible coupling mechanism is generally proposed for polymerizations in the presence of bis(acetylacetonate)cobalt(II) complexes. The process has been applied to VAc miniemulsion polymerization[77] and in the synthesis of poly(vinyl acetate)-*block*-poly(vinyl pyrrolidone) (PVAc-*b*-PNVP)[78,79] and PVAc-*b*-PSt.[80] Cobalt-mediated St polymerization is not believed to involve a reversible deactivation mechanism but rather is believed to be a conventional polymerization initiated by the PVAc organocobalt species.

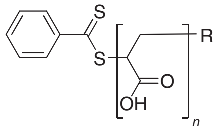
Ab initio calculations have been used as a tool in the design of thioketones as spin traps for controlling radical polymerization by an addition–fragmentation process.[81] The thiofluorenone **18** was proposed as a compound suitable for investigation with high radical affinity, appropriate addition–fragmentation equilibrium constant, and a low propensity to undergo copolymerization (Table 2). The diarylthioketone **20** was found to offer some control over BA polymerization.[82]

The thiolactone **19** was proposed to control the polymerization of St by a similar addition–fragmentation process (Scheme 2).[83] The mechanism as shown seems unlikely since, for control, most of the propagating species would need to be present as the dormant species **21**. ESR experiments showed that

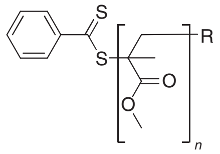
Table 1. Transfer and rate coefficients for RAFT agents in RAFT polymerization



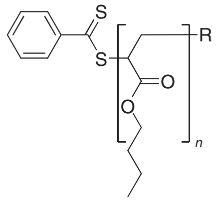
5 PSt



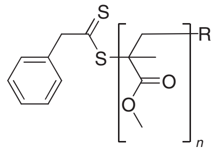
6 PAA



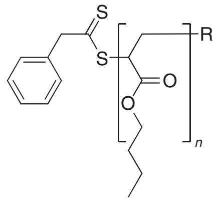
7 PMMA



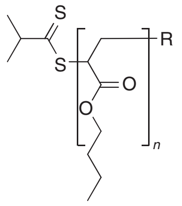
8 PBA



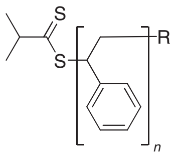
9 PMMA



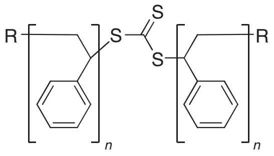
10 PBA



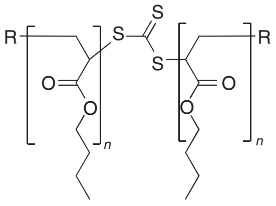
11 PBA



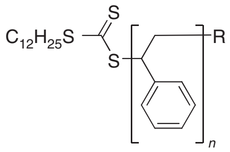
12 PSt



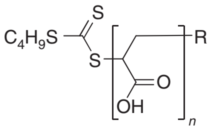
13 PSt



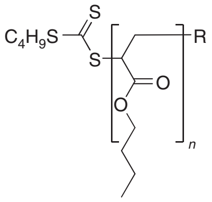
14 PBA



15 PSt



16 PAA



17 PBA

Agent	Z	R	Monomer	T [°C]	$C_{\mathrm{tr}}^{\mathrm{app\ A}}$	C_{tr}	$C_{-\mathrm{tr}}$	Ref.
7	Ph	PMMA	MMA	60	140	140	140	[62,63]
7	Ph	PMMA	BA	60	482	–	–	[62]
8	Ph	PBA	MMA	60	5	–	–	[62]
8	Ph	PBA	BA	60	~248	~248	~248	[62]
9	$PhCH_2$	PMMA	MMA	60	11	11	11	[62]
9	$PhCH_2$	PMMA	BA	60	205	–	–	[62]
10	$PhCH_2$	PBA	MMA	60	2.6	–	–	[62]
10	$PhCH_2$	PBA	BA	60	116	116	116	[62]
12	$(CH_3)_2CH$	PSt	St	60	42	42	42	[62]
12	$(CH_3)_2CH$	PSt	BA	60	54	–	–	[62]
11	$(CH_3)_2CH$	PBA	St	60	50	–	–	[62]
11	$(CH_3)_2CH$	PBA	BA	60	59	59	59	[62]
61	Ph	CH_2Ph	MMA	80	0.2	–	–	[64]
25	Ph	$C(CH_3)_3$	MMA	80	0.7	–	–	[64]
24	Ph	$C(CH_3)(CN)$	MMA	80	40	–	–	[64]
39	Ph	$C(CH_3)(CN)CH_2CH_2CO_2H$	MMA	80	>50	–	–	[64]
7	Ph	PMMA	MMA	80	>500	–	–	[64]
49	Ph	$CH(Ph)(CH_3)$	MMA	60	–	40–280	9900	[65]

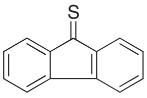
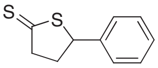
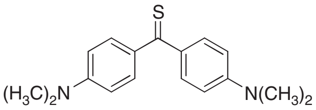
(*Continued*)

Table 1. (Continued)

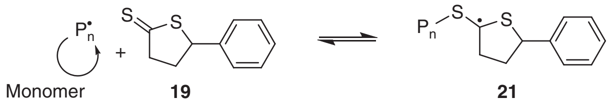
Agent	Z	R	Monomer	T [°C]	$C_{tr}^{app\ A}$	C_{tr}	C_{-tr}	Ref.
23	Ph	$C(CH_3)(C_2H_5)(CN)$	DEGMA	70	0.5			[66]
23	Ph	$C(CH_3)(C_2H_5)(CN)$	PEGMA	70	0.5			[66]
22	Ph	$C(Ph)(CH_3)_2$	St	120	–	2037	34	[67]
49	Ph	$CH(Ph)(CH_3)$	St	120	–	3331	4173	[67]
61	Ph	CH_2Ph	St	120	–	92	1057	[67,68]
61	Ph	CH_2Ph	St	60	190	–	–	[69]
5	Ph	PSt	St	60	$>10^3$	–	–	[69]
6	Ph	PAA	AA	70	8.3	–	–	[60]
16	SC_4H_9	PAA	AA	70	16.7	–	–	[60]
17	SC_4H_9	PBA	BA	70	34.5	–	–	[60]
15	$SC_{12}H_{25}$	PSt	St	70	143	–	–	[60]
110	SCH_2Ph	CH_2Ph	St	80	53	–	–	[70]
110	SCH_2Ph	CH_2Ph	BA	80	190	–	–	[70]
13	S(PS)	PSt	St	40	$>10^3$	–	–	[70]
14	S(PBA)	PBA	BA	40	220	–	–	[70]
103	$SC(CH_3)_2(CO_2H)$	$C(CH_3)_2(CO_2H)$	St	70	23.2	–	–	[71]
110	SCH_2Ph	CH_2Ph	St	70	19	–	–	[71]
130	$SCH_2CH_2CO_2H$	$C(CH_3)_2(CO_2H)$	St	70	20.2	–	–	[71]
156	$SCH_2CH_2CO_2H$	$CH(CH_3)(CO_2H)$	St	70	13.9	–	–	[71]
117	$SCH_2CH_2CO_2H$	$CH_2CH_2CO_2H$	St	70	4.32	–	–	[71]
212	OC_2H_5	$CH(CH_3)(CO_2CH_3)$	St	50–70	0.7	–	–	[72]
240	1-Pyrrole	$CH(Ph)(CH_3)$	St	80	82	–	–	[73]

[A] Published values of transfer constants that are based on a model that does not allow for partitioning of the intermediate radicals and/or the reversibility of chain transfer are considered as apparent transfer constants (see text). For macro-RAFT agents in homopolymerization, it is assumed that $C_{tr}^{app} = C_{tr} = C_{-tr}$.

Table 2. Thiocarbonyl spin traps

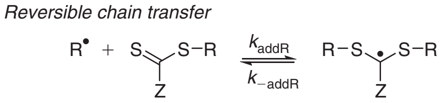
Spin trap[A]	Polymerizations
 **18**[81]	
 **19**[83]	St[83]
 **20**[82]	BA[82]

[A] Reference after compound number (where given) provides a synthesis of the spin trap.



Scheme 2. Reversible addition–fragmentation mechanism for dithiolactone.

a high concentration of radicals were not present during polymerization. The mechanism would suggest that the final product should also have structure **21**.



Scheme 3.

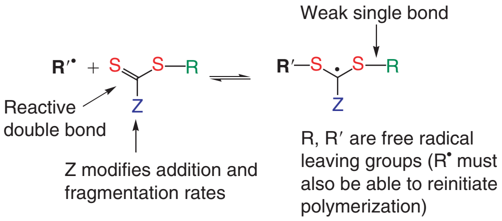


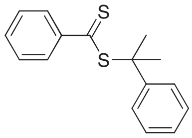
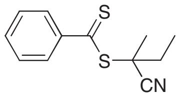
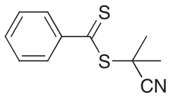
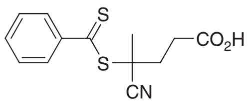
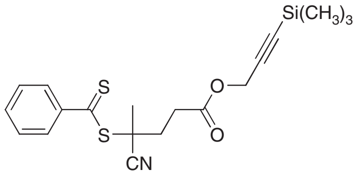
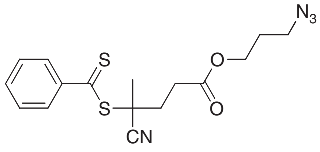
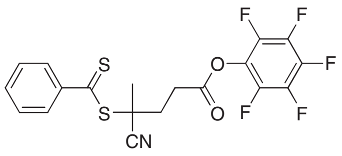
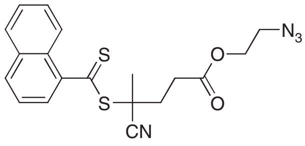
Fig. 3. Structural features of thiocarbonylthio RAFT agent and the intermediate formed on radical addition.

Choice of RAFT Agents

A wide variety of thiocarbonylthio RAFT agents (ZC(=S)SR, **1**) have been reported. A broad summary of these and the factors that influence the choice of RAFT agent for a particular polymerization was presented in previous reviews.[1,7,12] The effectiveness of the RAFT agent depends on the monomer being polymerized and is determined by the properties of the free radical leaving group R and the group Z, which can be chosen to activate or deactivate the thiocarbonyl double bond of the RAFT agent **1** and modify the stability of the intermediate radicals **2** and **4**. For an efficient RAFT polymerization (Scheme 1, Fig. 3):

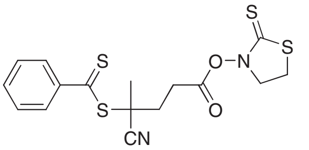
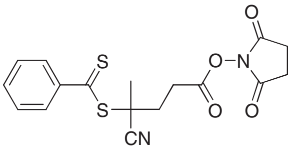
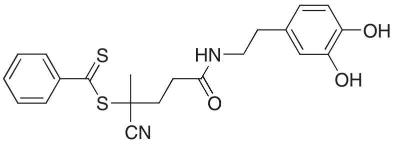
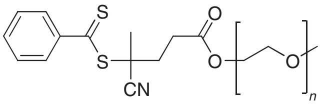
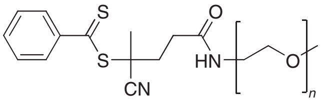
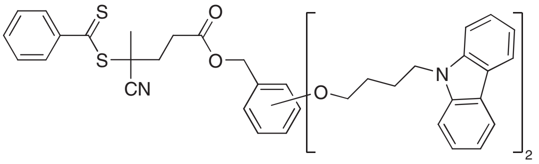
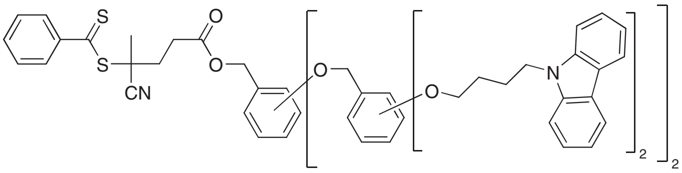
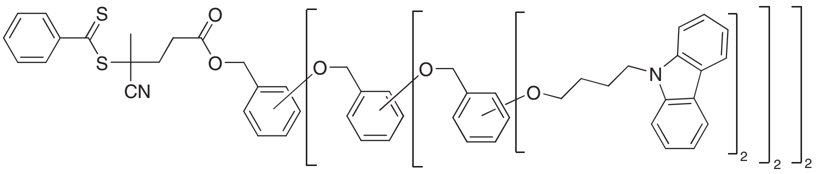
- The initial RAFT agents **1** and the polymer RAFT agent **3** should have a reactive C=S double bond (high k_{add}).
- The intermediate radicals **2** and **4** should fragment rapidly (high k_β, weak S–R bond in the intermediate) and give no side reactions.

Table 3. RAFT agents and RAFT polymerizations – aromatic dithioester RAFT agents (Z = aryl)

RAFT agent[A]	Polymerizations[B]
 **22***[86]	MA[54] AAEMA[87] MAEP[87] MMA[88,89] AEMA[90] DMAEMA[91] (TPMMA)[92] TFPMA[93] St[48,94,95] **277**[96] **278**[96] **392**[97,98] **345**[99] **348**[100] **347**[101] St[51] **364**[102] **365**[102] NVP[103] **385**[104] **386**[98] **387**[104] **388**[104] **389**[104] **390**[104] *BA/**407***[105] St/MAH[53] AAEMA-*b*-AEP[87] AAEMA-*b*-MAEP[87] MAEP-*b*-AAEMA[87] BMA/TMSEMA[106] TFPMA-*b*-tBA[93] St-*b*-NIPAM[95] St-*b*-HEMA/DMAEMA[86] **364**-*b*-**384**[102] **365**-*b*-**384**[102] **386**-*b*-**392**[97]
 **23***[107]	DEGMA[108] EGMA[108] MAA[108] MMA[109] PEGMA[108] **282**[110] **371**[111] **417**[112] St[107] DMAEMA/PEGMA[113] MAA/PEGMA[108] MMA/**371**[111] MMA-*b*-**371**[111] MMA/DMAEMA[114] MMA-*b*-DMAEMA[114] DEGMA/PEGMA[66]
 **24***[115]	BA[62] MA[54] (iBMA)[115] MMA[27,64,88,116–122] GMA[123] **280**[124] **281**[124] **294**[125] **295**[126] (**296**)[127] **306**[128] **307**[128] **308**[128] AN[129] DEAM[130] NIPAM[131,132] tBS[133] St[51,117] **363**[134] **370**[135] **371**[135] **375**[136] GMA-*b*-PFS[123] MMA-*b*-St[117] ***280***-*b*-*BMA*[124] ***281***-*b*-*BMA*[124] MMA-*b*-BA[118] HMA/**306**[128] LMA/**306**[128] HMA/**308**[128] LMA/**308**[128] MMA/**314**[137] MMA/**315**[137] MA/**314**[137] MA/**315**[137] MA/**317**[137] MA/**316**[137] St/MAH[53] St/**349**[138] MMA/BA[62] MMA/**296**[127] NIPAM-*b*-DEAM[131] HS-*b*-St[133]
 **25***[34]	BMA[139] MAA[140] MMA[64,141] AEMA[90,142] DEGMA[141] DMAEMA[143] DPAEMA[144] MAA[145] PEGMA[144,146–148] **383**[149] DMAM[150] NIPAM[151] **274**[152,153] **325**[154] **326**[154] APMAM-*b*-NIPAM[89,152] AEMAM[153] St[155] **274**[153] **275**[153] **285**[156] **286**[156] **289**[157] **292**[158] **304**[140] **305**[140] **331**[159] **329**[140] **327**[157] **380**[160] **391**[161,162] **389**[104] (**390**)[104] **416**[163,164] *MAA-b-**280***[145] BMA-*b*-MPC[139] PEGMA/**320**[165] PEGMA/**344**[165] DEGMA-*b*-**384**[141] MMA-*b*-**384**[141] DMAEMA-*b*-NIPAM[143] DPAEMA-*b*-PEGMA PEGMA/AMPS[147,148] PEGMA-*b*-AMPS[147,148] PEGMA-*b*-**370**[146] **383**-*b*-LMA[149] **275**-*b*-**274**[153] NIPAM[166] SSO3Na[167] **285**-*b*-BMA[156] **286**-*b*-DMAEMA[156] **286**-*b*-BA[156] **289**-*b*-**327**[157] **304**-*b*-MAA[140] MAA-*b*-**304**[140] MAA-*b*-**305**[140] MMA-*b*-**304**[140] MMA-*b*-**305**[140] DMAM-*b*-NIPAM/**377**[150] NIPAM-*b*-**276**[166] NIPAM/**274**[153] MPC/**275**[153] HPMAM/APMAM[168] **391-***b*-HPMAM[161] HPMAM/APMAM-*b*-DMAPMAM[168] St-*b*-**384**[155] **292**-*b*-DEAM[158] **292**-*b*-VBA[158] **292**-*b*-**293**[158] **292**-*b*-**350**[158] **325**-*b*-AEMAM[154] **325**-*b*-MPC[154] **326**-*b*-AEMAM[154] **326**-*b*-APMAM[154] APMAM-*b*-**326**[154] **329**-*b*-AM[140] **380**-*b*-AM[160]
 **26**[169]	St[169] **287**[170]
 **27**[171]	St[169,171,172] DMAM[171] St-*b*-DMAM[171] DMAM-*b*-St[171]
 **28**[173]	DEGMA[173] LMA[89,173] MMA[173] PEGMA[89,173] NIPMAM[173]
 **29**[174]	St[174]

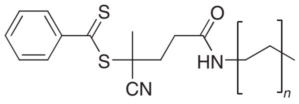
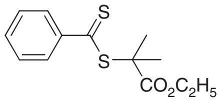
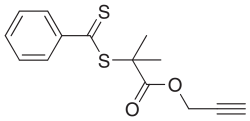
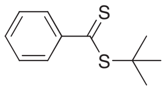
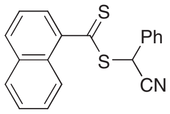
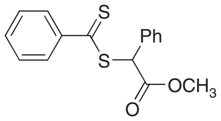
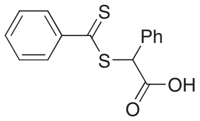
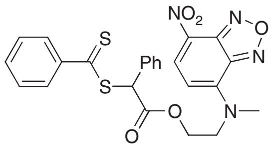
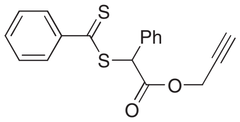
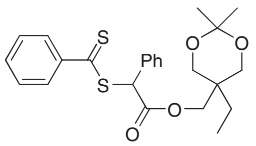
(*Continued*)

Table 3. (Continued)

RAFT agent[A]	Polymerizations[B]
 **30**[175,176]	–[C]
 **31**[177–179]	**381**[178] [C]
 **32**[176]	St[176]
 **33***[180] PEO macro-RAFT agent	St[180]
 **34**[181] PEO macro-RAFT agent	St[181]
 **35**[182] G1 dendron RAFT agent[D] (*ar*-3,5-substitution)	St[182] MMA[182]
 **36**[182] G2 dendron RAFT agent[D] (*ar*-3,5-substitution)	MMA[182]
 **37**[182] G3 dendron RAFT agent[D] (*ar*-3,5-substitution)	MMA[182]

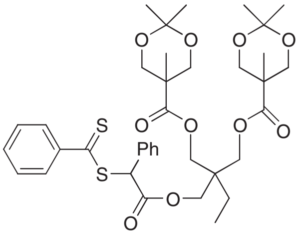
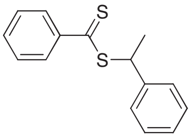
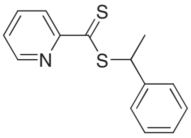
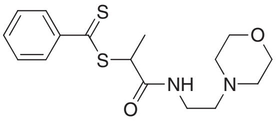
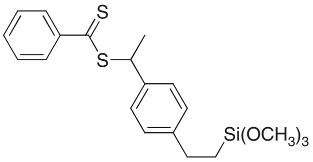
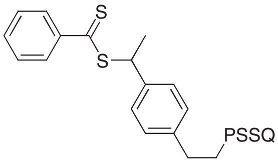
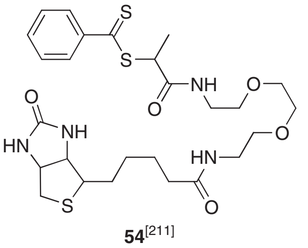
(*Continued*)

Table 3. (Continued)

RAFT agent[A]	Polymerizations[B]
 **38**[177] PE macro-RAFT agent	BA[177]
 **39***[183]	St[184] MMA[88] **323**[185]
 **40**[186]	St[186] St-*b*-MAH[186] St-*b*-MAH-*b*-NIPAM[186]
 **41***[187,188]	(MMA)[64,187,189] BA[187] EHA[188] St[190] TBAM[191] DEAM[187] DMAM[187] NAM[191] NIPAM[187,189] BA/St[192] *EHA-b-MA*[188] TBAM-*b*-NAM[191] DMAM/NAS[193] NAM-*b*-TBAM[191]
 **42***	MMA[194] **376**[195] **376**-*b*-MMA[195]
 **43***	BA[196] MMA[189] NIPAM[189] MMA-*b*-NIPAM[189] MMA/**283**[197] MMA/**284**[197] St/2VP[198] St/**348**[199] THPA-*b*-St[200] THPA-*b*-St/**373**[201]
 **44**[202]	–[C]
 **45**[44]	BA[44]
 **46**	THPA-*b*-St[200]
 **47**[203] G1 dendron RAFT agent[D]	MMA[203] **303**[203]

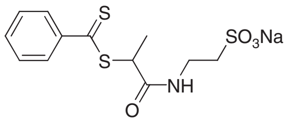
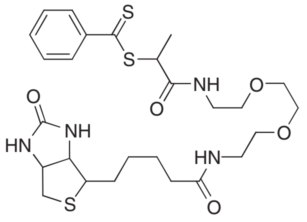
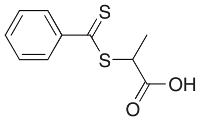
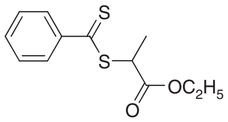
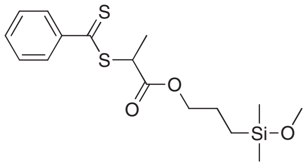
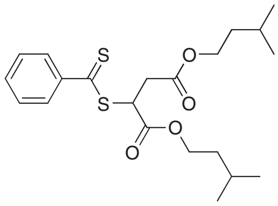
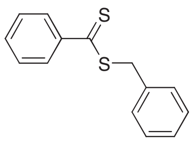
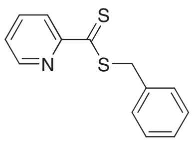
(*Continued*)

Table 3. (Continued)

RAFT agent[A]	Polymerizations[B]
 **48**[203] G2 dendron RAFT agent[D]	MMA[203] **303**[203] St[203]
 **49***	PEGA[204] St[205] **357**[206] **362**[207] St/EVE[208] (St/MAH)[208]
 **50**[209]	
 **51**	NAM[47]
 **52**[210]	–[C]
 **53**[210][E] Poly(silsesquioxane) macro-RAFT agent	MMA[210] MA[210] DMAM[210] St[210] MMA/**312**[210]
 **54**[211]	NAM[211]

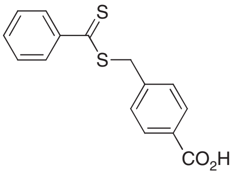
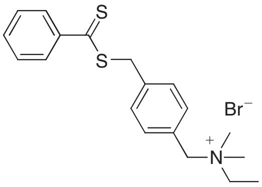
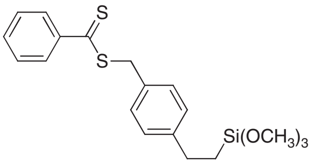
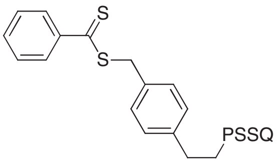
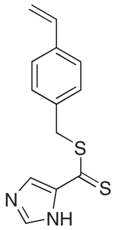
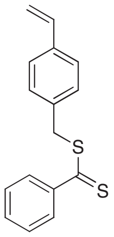
(*Continued*)

Table 3. (Continued)

RAFT agent[A]	Polymerizations[B]
 **55**	PEGMA/**344**[165]
 **56**[211,212]	NAM[47,211] NAM/**342**[212]
 **57***	AA[60]
 **58***	BA[213] PEGA[204] St[46,213] SSO3Na/PEGMA[214]
 **59**	—[C]
 **60**[215]	DcAM[215]
 **61***	*BA*[216] PEGA[217] (MMA)[64] St[51,68,69,89,218] DMAM[218] NIPAM[219] (NVPI)[220] **332**[221] **336**[221] **338**[221] **382**[222] PEGA-*b*-NIPAM[217] (St-*b*-DMAM)[218]
 **62***	iBA[223] St[223,224] **385**[104] **388**[104] **389**[104]

(*Continued*)

Table 3. (Continued)

RAFT agent[A]	Polymerizations[B]
 **63***	MAA[225] *MAA-b-St*[225]
 **64**[226,227]	St[226]
 **65**[210]	–[C]
 **66**[210,228] Poly(silsesquioxane) macro-RAFT agent	MA[210] EHA[210] NIPAM[228] MA/**324**[210] [E]
 **67**	NIPAM[229]
 **68***[230]	St[230]

(*Continued*)

Table 3. (Continued)

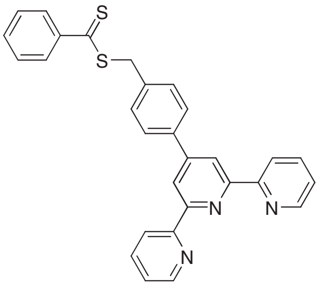
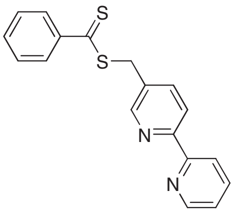
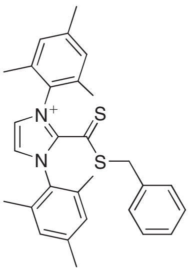
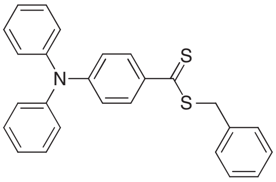
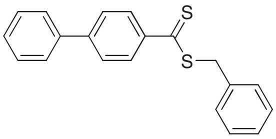
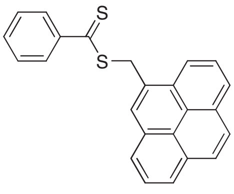
RAFT agent[A]	Polymerizations[B]
 **69**[45]	St[45]
 **70**[45,231]	St[45,231] NIPAM[231,232]
 **71**[233]	St[233]
 **72**[234]	St[234] MA[234] St-*b*-MA[234]
 **73**[235]	tBA[235] tBA-*b*-**338**[235]
 **74**[236]	St[236]

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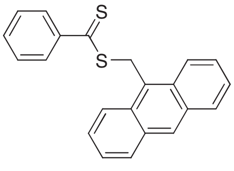
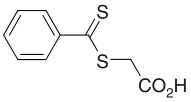
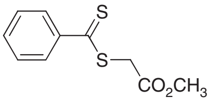
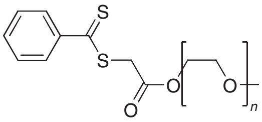
Table 3. (Continued)

RAFT agent[A]	Polymerizations[B]
 **75**[237]	St[237]
 **76***	MAA[238] (MMA)[187] BA[187] AM[239] **341**[239] AM/**341**[239] AM/**340**[239] (DEAM)[187] (DMAM)[187] (NIPAM)[187] NIPAM[238] NIPAM-*b*-MAA[238]
 **77**[187]	(MMA)[187] BA[187] DEAM[187] DMAM[187] (NIPAM)[187]
 **78**[187] PEO macro-RAFT agent	(MMA)[187] BA[187] DEAM[187] DMAM[187] (NIPAM)[187]

[A] Reference after compound number (where given) provides a synthesis of the RAFT agent. An asterisk indicates the RAFT agent is mentioned in our previous reviews[7,8] or has been previously described.

[B] If a monomer appears in italics the polymerization was performed in heterogeneous media (emulsion, miniemulsion, dispersion). If a monomer appears in parentheses, a relatively broad molecular weight distribution ($Đ > 1.4$) and/or significant retardation/inhibition was observed. Note that this does not mean an absence of control. Polymerizations leading to statistical copolymers are designated as A/B. Polymerizations leading to block copolymers are designated as A-*b*-B. The first mentioned monomer (A) was polymerized first and the polymer formed used as a macro-RAFT agent in polymerization of the second mentioned monomer (B).

[C] Compounds not used as RAFT agents directly but served as precursors to other RAFT agents.

[D] Higher generation dendron RAFT agents were also reported.

[E] PSSQ = poly(silsesquioxane).

- The intermediate **2** should partition in favour of products ($k_\beta \geq k_{-\mathrm{add}}$).
- The expelled radicals ($R^\bullet$) must efficiently re-initiate the polymerization ($k_i > k_p$).

The properties of RAFT agents are often discussed in terms of the value of the equilibrium constants (K) associated with radical addition to the thiocarbonylthio compound. Rates of addition are typically high (k_{add} $\sim 10^6$–10^8 M^{-1} s^{-1}). Thus a high equilibrium constant generally implies a low fragmentation rate for the radical adduct and an increased likelihood for retardation and/or side reaction involving this species. Values of K do not, by themselves, provide sufficient information to predict the ability of a RAFT agent to control polymerization.

In a given RAFT polymerization, there are at least four equilibrium constants that need to be considered.

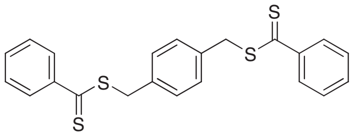
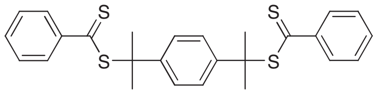
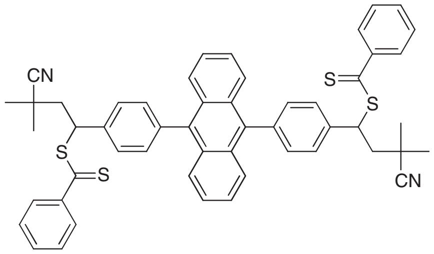
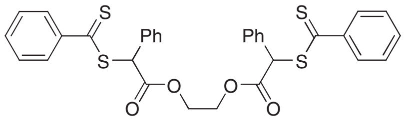
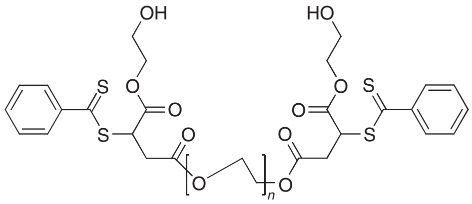
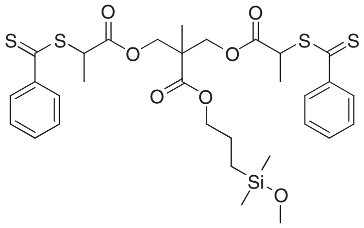
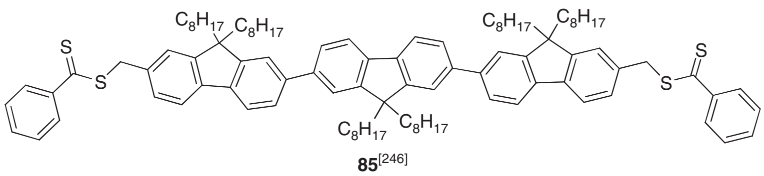
- K_P ($= k_{\mathrm{addP}}/k_{-\mathrm{addP}}$) associated with the main equilibrium.
- K ($= k_{\mathrm{add}}/k_{-\mathrm{add}}$) and $K_\beta = (k_{-\beta}/k_\beta)$ associated with the pre-equilibrium.
- K_R ($= k_{\mathrm{addR}}/k_{-\mathrm{addR}}$) associated with the reaction of the expelled radical with the initial RAFT agent (Scheme 3).

There are other equilibrium constants to consider if penultimate group effects are significant. *Ab initio* methods have been used for the prediction and rationalization of substituent effects on RAFT agent activity.[16,84]

A summary of 'new' RAFT agents and new polymerizations in which they and pre-existing RAFT agents have been applied are shown in Tables 3–15. The tables include some RAFT agent/monomer combinations that provide poorer molecular weight control and/or dispersity $Đ_M > 1.4$. These are generally indicated by the monomer being in parentheses. Often these have been investigated in order to provide an understanding of the mechanism and to allow construction of guidelines for the choice of RAFT agent.

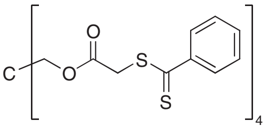
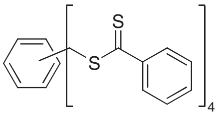
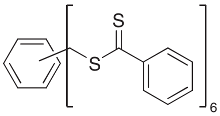
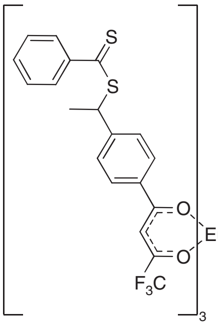
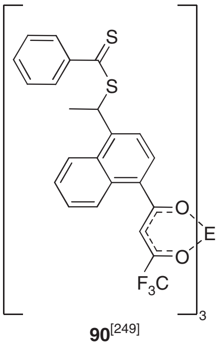
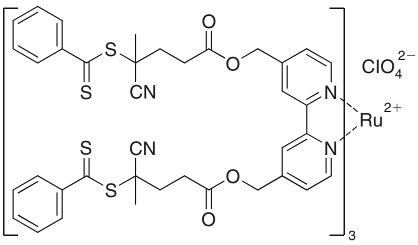
The data included in Tables 3–15 show that tertiary-dithiobenzoates (in particular, **22**–**32**) continue to be the most popular RAFT agents for synthesizing polymers based on 1,1-disubsituted methacrylate or methacrylamide monomers. The use of the corresponding trithiocarbonates **118**–**125** has also been promoted in this context.[27] Secondary aromatic dithioesters with R = –CHPh(CN) (**42**) and –CHPh(CO_2R) (**43**–**48**) and analogous trithiocarbonates **144**, **145**, and **146**–**148**, respectively, have been shown to have utility in controlling

Table 4. Multi-RAFT agents and RAFT polymerizations – aromatic dithioester RAFT agents (Z = aryl)

RAFT agent[A]	Polymerizations[B]
'R'-connected	
 **79***[227]	NIPAM[240]
 **80***[86,241,242]	BMA[243] DMAEMA[240–243] AA[241] BA[243] St[241,243] DMAEMA-*b*-BMA[243] DMAEMA-*b*-BA[243] DMAEMA-*b*-St[243] St-*b*-HEMA/DMAEMA[86]
 **81**[244]	**358**[244]
 **82**[202]	MMA[196,202] MMA-*b*-BMA[202] MMA-*b*-BA[196,202]
 **83**[245] PEO macro-RAFT agent	St[245]
 **84**[213]	C
 **85**[246]	NIPAM[246]

(*Continued*)

Table 4. (Continued)

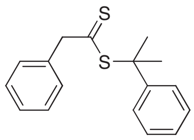
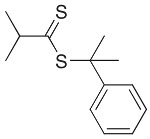
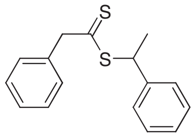
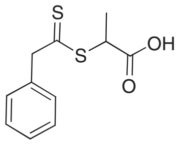
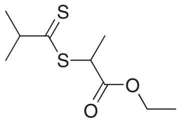
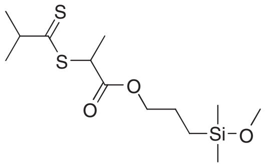
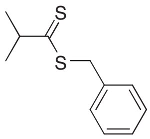
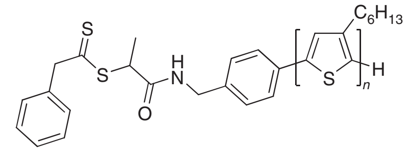
RAFT agent[A]	Polymerizations[B]
 **86**[247]	St[247] (MMA)[247] (St-*b*-DMAEMA)[247]
 **87***	St[248]
 **88***	St[248]
 **89**[249]	SB[249] SB-*b*-St[249]
 **90**[249]	St/SB[249] St/SB-*b*-MMA[249]
 **91***	**361**[250] **361**-*b*-NIPAM[250]

[A] See footnote A of Table 3.

[B] See footnote B of Table 3. In the case of bis-RAFT agents sequential polymerization of two monomers will yield a triblock.

[C] See footnote C of Table 3.

Table 5. RAFT agents and RAFT polymerizations – dithioester RAFT agents (Z = alkyl or aralkyl)

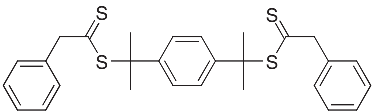
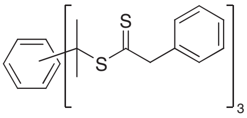
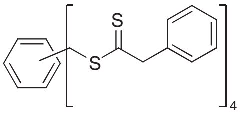
RAFT agent[A]	Polymerizations[B]
 **92***	AA[251] BA[251,252] *BA*[253] MA[54,252] St[254,255] HPA[251] St[256] SMe[251] BP/NPMI[257]
 **93**[216]	BA[216] (*BA*)[216]
 **94***[255]	AEP[87] BA[62,216] (*BA*)[216] TFPA[93] *MMBL*[258] AcS[259] St[260] St[261] PFS[93] NIPAM[262,263] St/MMBL[258] MMA/BA[62] BP/NPMI[257] BP/NMMI[257] BP/NEMI[257] TFPA-*b*-tBA[93] PFS-*b*-tBA[93]
 **95**[264]	C
 **96**[213]	BA[213]
 **97**[213]	C
 **98***[265]	BA[62,216,265] *BA*[216] St[265] St/BA[265,266]
 **99**[264] Poly(3-hexylthiophene) macro-RAFT agent	**313**[264]

[A] See footnote A of Table 3.

[B] See footnote B of Table 3.

[C] Compounds not used as RAFT agents directly but served as precursors to other RAFT agents.

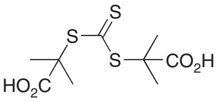
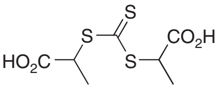
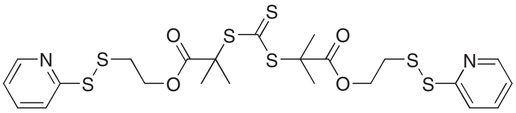
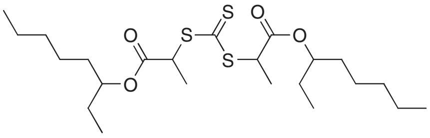
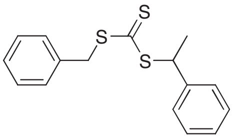
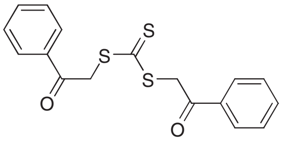
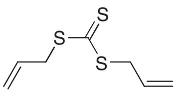
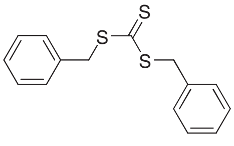
Table 6. Multi-RAFT agents and RAFT polymerizations – aromatic dithioester RAFT agents (Z = alkyl or aralkyl)

RAFT agent[A]	Polymerizations[B]
'R'-connected	
 **100**[260]	St[260]
 **101**[248] *ar*-1,3,5-substitution	St[267]
 **102**[248] *ar*-1,2,4,6-substitution	MA[268] AcS[259] St[248]

[A] See footnote A of Table 3.

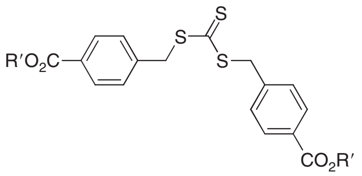
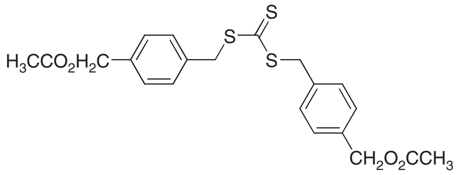
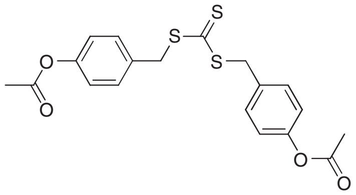
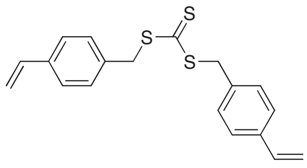
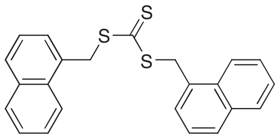
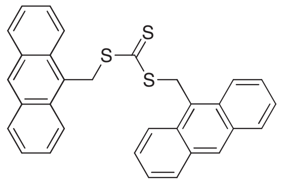
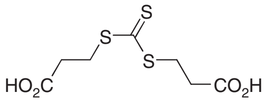
[B] See footnote B of Table 3. In the case of bis-RAFT agents sequential polymerization of two monomers will yield a triblock.

Table 7. RAFT agents and RAFT polymerizations – symmetric trithiocarbonate RAFT agents

RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **103***	AA[269] BA[270] MA[270] NIPAM[269,271–273] **420**[274] St[71,275] 2VP[276] NVP[103] NIPAM/**274**[153] TMAPMA/PEGMA/NIPAM[277] (PEGMA/**320**)[165] (PEGMA/**344**)[165] **331**[159] AEMA/**325**/**328**[278] DMAM-*b*-**331**[159] DMAM-*b*-**331**-*b*-NIPAM[159] NIPAM-*b*-DMAM[272] 2VP-*b*-EA[276] AEME/**328**/**342**[278]	 **104***[279,280]	BA[281] DA[281] DEHEA[280] MA[281] tBA[280] BA/AA[279] DEHEA-*b*-ODA[280] DEHEA-*b*-tBA[280] tBA-*b*-DEHEA[280]
 **105**[282]			PEGA[282] PEGA-*b*-St[282]
 **106**[188]			EHA[188] *EHA-b-MA*[188]
 **107**[283]C		 **108**[275]	St[71,275] (St-*b*-BA)[275]
 **109**[284]	tBA[284] St[284] tBA-*b*-St[284] St-*b*-BA[284]	 **110***[283]	BA[70] tBA[283] AM[285] St[70,286] St-*b*-NIPAM[286] St/AA[287] St/AA-*b*-St[287] St/MAH/NVP[288,289]

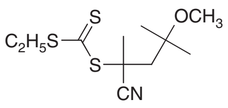
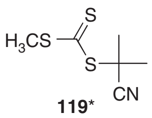
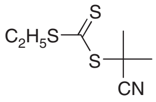
(*Continued*)

Table 7. (Continued)

RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **111a** R′ = CH_3[290] **111b** R′ = C_2H_5[290] **111c** R′ = iC_3H_7[290] **111d** R′ = tC_4H_9[290] **111e** R′ = CH_2Ph[290]		 **112**[290]	
 **113**[290]		 **114**[290]	
 **115**[291,292]	St[291,292] St-*b*-NIPAM[291]	 **116**[292]	St[292]
 **117**	(St)[71]		

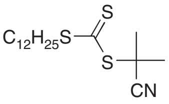
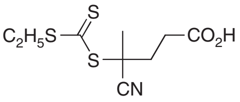
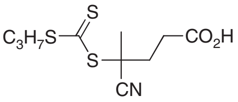
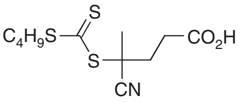
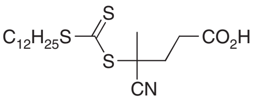
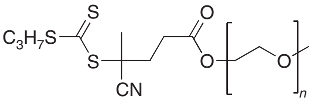
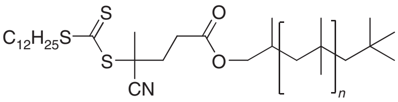
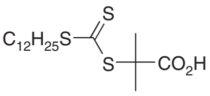
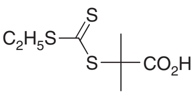
[A] See footnote A of Table 3.
[B] See footnote B of Table 3.
[C] Included here because of two radical leaving groups.

Table 8. RAFT agents and RAFT polymerizations – non-symmetric trithiocarbonate RAFT agents

RAFT agent[A]	Polymerizations[B]
 **118**	(TPMMA)[92]
 **119***	MMA[27,88,121]
 **120**	(TPMMA)[92]

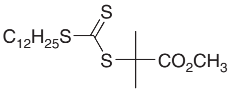
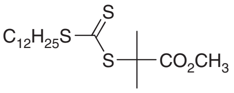
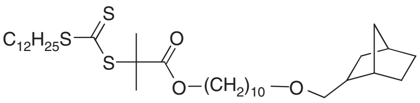
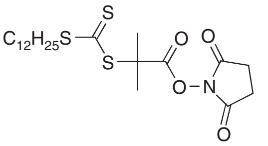
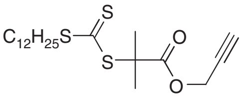
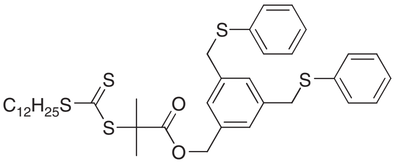
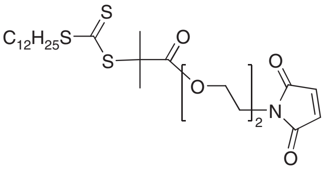
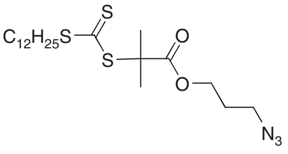
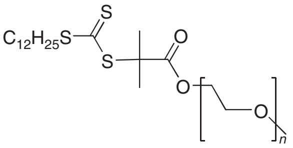
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **121**[94]	MMA[94] St[51]
 **122**[293]	DMAEMA[293] DMAEMA-*b*-AA/BMA/DMAEMA[293]
 **123**[294]	–[C]
 **124**	MMA[27]
 **125***	MMA[27] MAA/CMA[295]
 **126**[294] PEO macro-RAFT agent	APMAM[294] APMAM-*b*-DPAEMA[294]
 **127**[296] PIB macro-RAFT agent	MMA[296] St[296]
 **128***[283]	AA[91] CA[297] tBA[298] MA[299] (BMA)[300] (*BMA*)[300] CMA[301] MMA[122,283] (MMA)[122] BAM[302] DEAM[302,303] DMAM[302,303] EMAM[302,303] NIPAM[302–306] PAM[302,306] MVK[307] PVK[307] **297**[308] tBS[276] CMS[309] HMS[309] St[91,300,309] (St)[300] 4VP[310] Ip[311] **320**[312] **325**[100] **327**[309] **331**[313] **332**[313] NVP[103] **331**-*b*-St[313] tBA-*b*-Ip[298] tBA-*b*-St[298] tBA-*b*-IP-*b*-St[298] tBA-*b*-St-*b*-IP[298] MA-*b*-NAS/MAM[299] (BMA/BA)[300] (*BMA/BA*)[300] (BMA/St)[300] (*BMA/St*)[300] MAH/Dc[314] MAH/Dc/VAc[314] MAH/Dc/MA[314] MAH/Dc/St[314] EHA/**297**[308] CMA-*b*-TMSEMA[301] St/MAH-*b*-Ip[315] StMAH-*b*-**332**[313] NVP-*b*-2VP[103] NIPAM/MAA[316] NIPAM/PAA[316] PAM-*b*-NIPAM[303,306] PAM-*b*-NIPAM-*b*-EMAM[303,306] NIPAM/NAS/**279**[317] **320**-*b*-NIPAM[312] St-*b*-CMS[309] CMS-*b*-HMS[309] 4VP-*b*-St[310] *4VP*-*b*-St[310] St-*b*-CA[297] Ip-*b*-St[311]
 **129***	DMAM[159] **330**[318] **331**[159,318] **339**[319] DMAM-*b*-**331**[159] DMAM-*b*-**331**-*b*-NIPAM[159] **331**-*b*-**330**[318] DMAM-*b*-NIPAM/**339**[319]

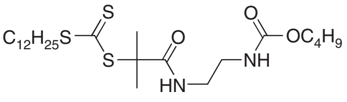
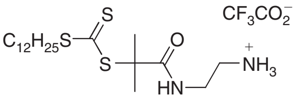
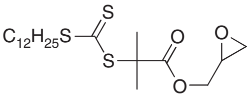
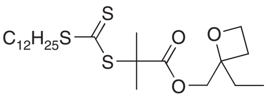
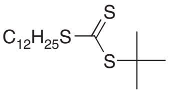
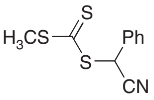
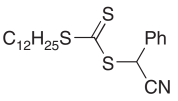
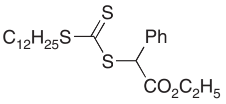
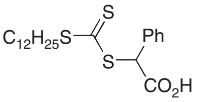
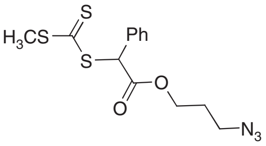
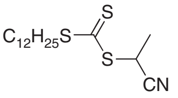
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **130***	NIPAM[304] St[71] NIPAM[320] NIPAM-*b*-VBA[320]
 **131**[321]	tBA[322] **353**[321] St/PFS[322] **353**/PFS[321] St/MAH[321] tBA-*b*-St/PFS[322] St/MAH-*b*-**353**/St[321] St/MAH-*b*-**353**/PFS[321]
 **132**[323]	–[C]
 **133**[324,325]	St[325]
 **134**[326,327] C	–[C]
 **135**[328]	MA[328] MA-*b*-tBA[328]
 **136**[329] C	–[C]
 **137**[30,171]	BA[330] St[171] DMAM[171] NIPAM[331] St-*b*-DMAM[171] DMAM-*b*-St[171] NIPAM-*b*-DMAM[332]
 **138**[333] PEO macro-RAFT agent	DEAM[333] DMAM[333] DMAM-*b*-DEAM[333] St[325]

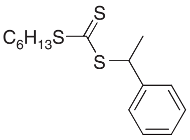
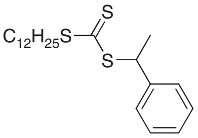
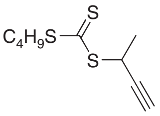
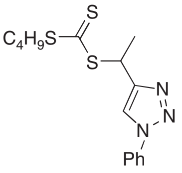
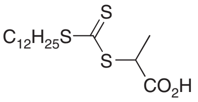
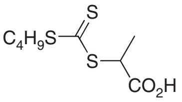
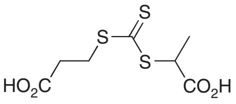
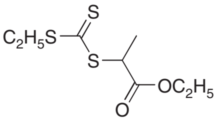
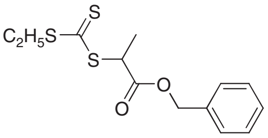
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **139**[324]	NIPAM[324]
 **140**[324]	–[C]
 **141**[334]	BMA[334] BA[334] EHA[334] LA[334] St[334] St-*b*-BA[334] BA-*b*-EHA[334] BA-*b*-LA[334]
 **142**[334]	BA[334] EHA[334] LA[334] St[334] BA-*b*-EHA[334] BA-*b*-LA[334]
 **143**[283]	–
 **144**[8]	MMA[8]
 **145**[27]	MMA[27]
 **146**[283]	tBA[283]
 **147**[27]	MMA[27]
 **148**[335]	NIPAM[335]
 **149**[283]	

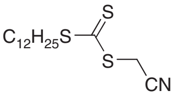
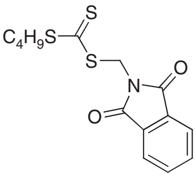
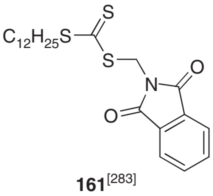
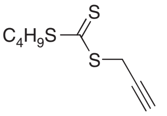
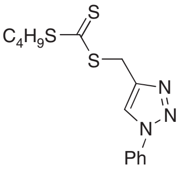
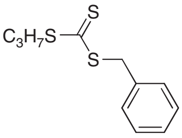
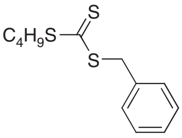
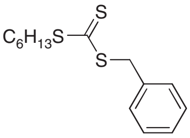
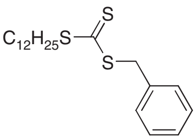
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **150**[336,337]	St[336,337] CMS[336]
 **151***[338]	(AA/CPA)[338] (AA/PA)[338]
 **152**[339]	–[C]
 **153**[339]	BA[339] St[339]
 **154***[340]	AA[341] BA[61] AA-*b*-BA[341] St[60] AA-*b*-St[341] TPSPMA[340]
 **155***	AA[60] BA[60] BA/AA[279]
 **156***[34]	St[71] *AM*[342,343] VBTPC-*b*-VBDA[34]
 **157**[344]*	EA[345] MA[344] EA-*b*-HEA/NAS[345]
 **158**[204]	PEGA[204]

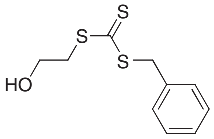
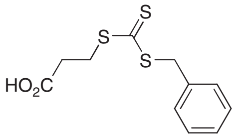
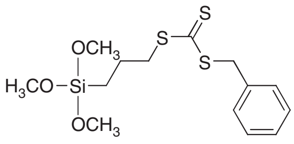
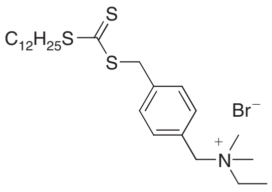
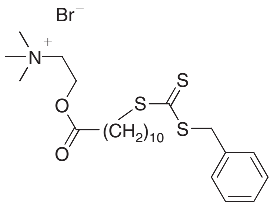
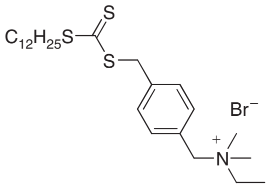
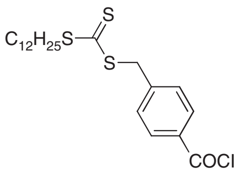
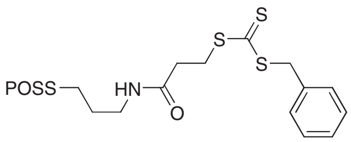
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **159**[94]	AA[251] BA[94,251] HEA[251] HPA[251] ODA[251] DMAM[251] NIPAM[251] St[94] SMe[251]
 **160***	AA/CPA[346] AA/PA[346] NIPAM/PA/NAS[347]
 **161**[283]	tBA[283]
 **162**[339]	_C
 **163**[339]	BA[339] St[339]
 **164**[348]	MA[349] **165**[350] St[350] St-*b*-MA[350]
 **166**[351]	(*BA*)[351] (St)[351] (St-*b*-BA)[351] (BA-*b*-St)[351]
 **167**[337]	St[337]
 **168***[352]	**319**[352]

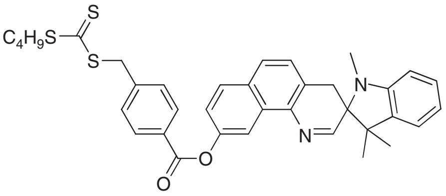
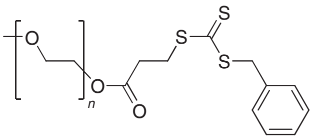
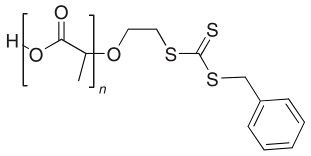
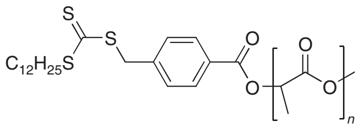
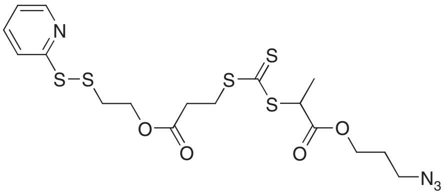
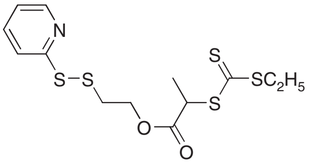
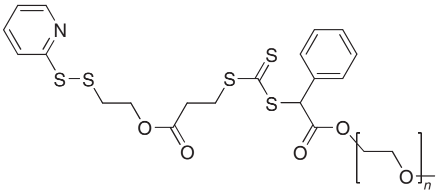
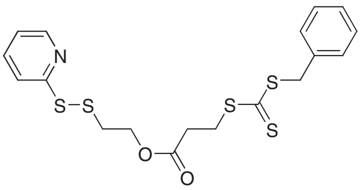
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **169**[283]	St[283,353]
 **170**[283]	AA[354] DMAM[218] NIPAM[355] St[218,283] (St)[356] (SSO3Na)[167] DADMAC[357] **346**[358] AA-*b*-SSO3Na[354] **346**-*b*-DMAM[358] (St-*b*-DMAM)[218]
 **171**[349]	MA[349] MA-*b*-St[349]
 **172**[226]	St[226]
 **173**[227]	–
 **174**[227]	–
 **175**[359]	–[C]
 **176**[350,360] POSS macro-RAFT agent	tBA[361] NIPAM[360] St[350] St-*b*-MA[350]

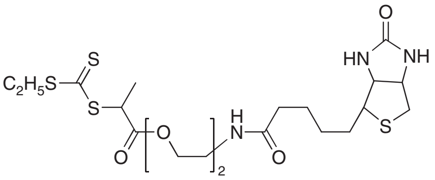
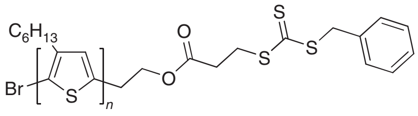
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **177**[362]	St[362] BA[362] St-*b*-BA[362] BA-*b*-St[362]
 **178**[363] PEO macro-RAFT agent	DMAPMAM/**419**[363]
 **179*** Poly(lactic acid) macro-RAFT agent	**319**[352]
 **180**[359] Poly(lactic acid) macro-RAFT agent	St[359]
 **181**[364]	NIPAM[364]
 **182**[365]	PEGA[365]
 **183**[366][C] PEO macro-RAFT agent	–[C]
 **184**[367][C]	–[C]

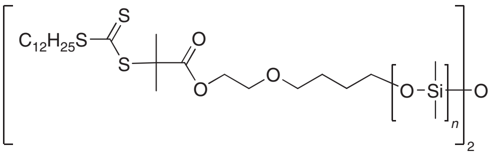
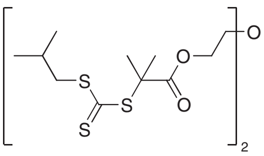
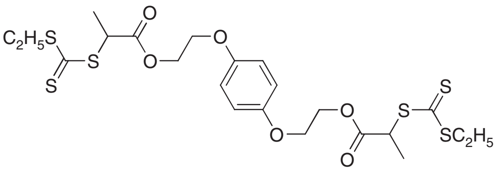
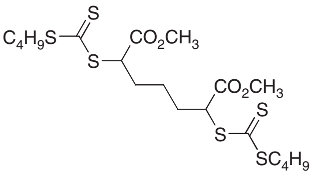
(*Continued*)

Table 8. (Continued)

RAFT agent[A]	Polymerizations[B]
 **185**[368]	NIPAM[368]
 **186**[369] Poly(3-hexylthiophene) macro-RAFT agent	St[369]

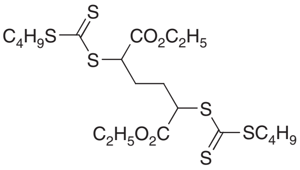
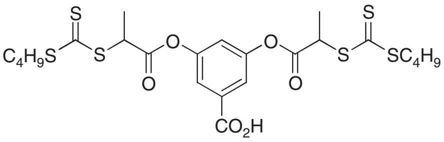
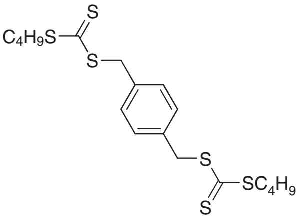
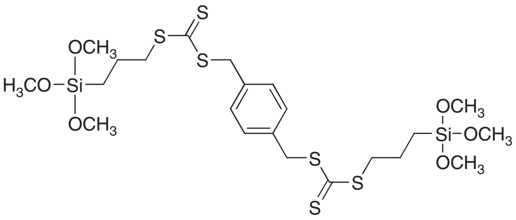
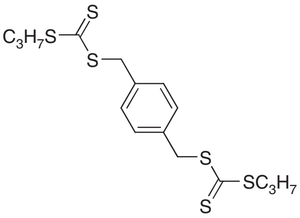
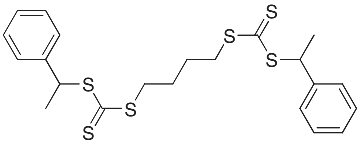
[A] See footnote A of Table 3.
[B] See footnote B of Table 3.
[C] Compounds not used as RAFT agents directly but served as precursors to other RAFT agents.

Table 9. Multi-RAFT agents and RAFT polymerizations – trithiocarbonate RAFT agents

RAFT agent[A]	Polymerizations[B]
‘R’-connected	
 **187**[370] Poly(dimethylsiloxane) macro-RAFT agent	DMAM[370] DMAM-*b*-HEA[370]
 **188**[371,372]	NIPAM[371–373]
 **189**[374]	NIPAM/**321**[374]
 **190**[286]	NIPAM[286] St[286] (NIPAM-*b*-St)[286] St-*b*-NIPAM[286]

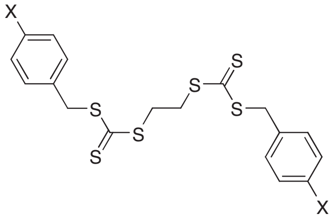
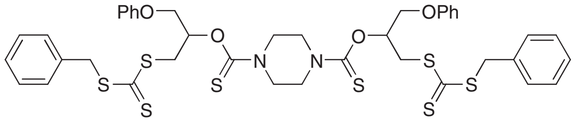
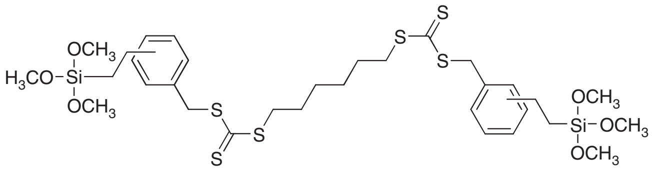
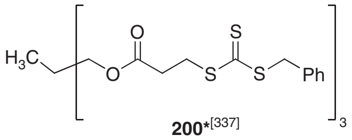
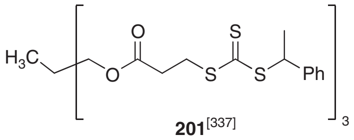
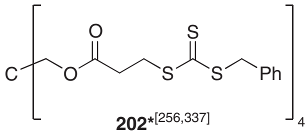
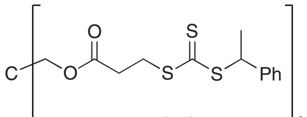
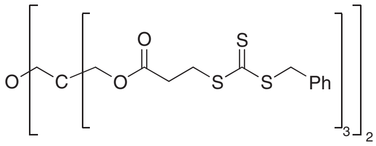
(*Continued*)

Table 9. (Continued)

RAFT agent[A]	Polymerizations[B]
'R'-connected	
 **191**[286]	NIPAM[286] St[286] (NIPAM-*b*-St)[286] St-*b*-NIPAM[286]
 **192**[375]	BA[375] St[375]
 **193**[351]	(*BA*)[351] (St)[351] (St-*b*-BA)[351] (BA-*b*-St)[351]
 **194**[348]	MA[349]
 **195**[286]	NIPAM[286] St[286] (NIPAM-*b*-St)[286] St-*b*-NIPAM[286]
'Z'-connected	
 **196**[336]	St[336] CMS[336] St-*b*-CMS[336] CMS-*b*-St[336]

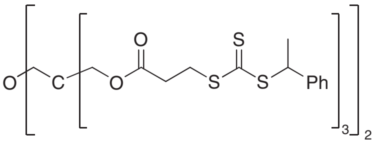
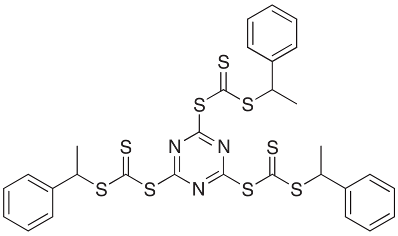
(*Continued*)

Table 9. (Continued)

RAFT agent[A]	Polymerizations[B]
‘R’-connected	
 **197** X = H, Cl, CF_3[286]	St[286] St-*b*-NIPAM[286]
 **198**[376]	St[376]
 **199**[348]	–[C]
 **200***[337]	St[337]
 **201**[337]	St[337]
 **202***[256,337]	St[256,337]
 **203**[337]	St[337]
 **204***[256,377]	St[256,337,377]

(*Continued*)

Table 9. (Continued)

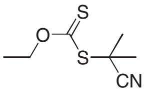
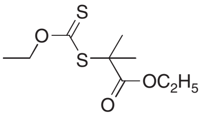
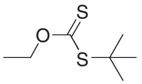
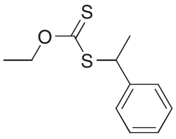
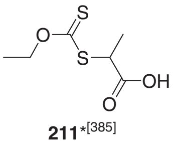
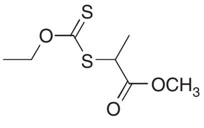
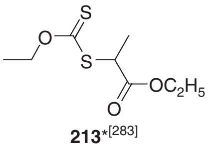
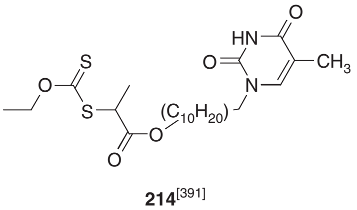
RAFT agent[A]	Polymerizations[B]
'R'-connected	
 **205**[337,377]	St[337,377]
 **206**[378]	St[378] St-*b*-NIPAM[378]

[A] See footnote A of Table 3.

[B] See footnote B of Table 3. In the case of bis-RAFT agents sequential polymerization of two monomers will yield a triblock.

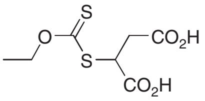
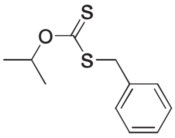
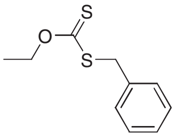
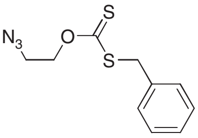
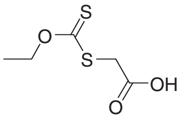
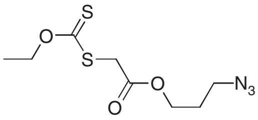
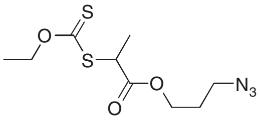
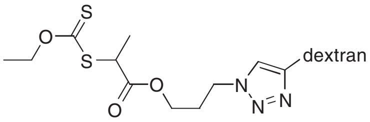
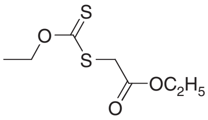
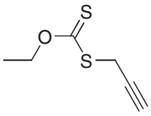
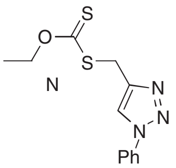
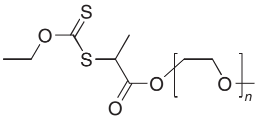
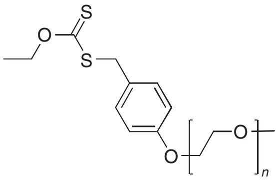
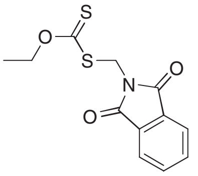
[C] Compounds not used as RAFT agents directly but served as precursors to other RAFT agents.

Table 10. RAFT agents and RAFT polymerizations – xanthate RAFT agents[A]

RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **207***	(VAc)[55] NVP[55,379] **366**[380] **367**[380] **368**[380]	 **208***	NVPI[220]
 **209**	(VAc)[55] (NVP)[55]	 **210***[283,381]	NVC[283,382,383] NVCL[384] NVP[381] NVPI[220] **366**[380] **367**[380] **368**[380] NVC-*b*-**310**[382] NVC-*b*-**311**[382] NVP-*b*-VAc[381]
 **211***[385]	VAc[55,385] NVP[55]	 **212**	(BA)[386] *BA*[387] (DEGMA)[386] *EHA*[387] St[72] VAc[388] (BA-*b*-AA)[386] (DEGMA-*b*-AA)[386]
 **213***[283]	St[72] VAc[389] VB[389] NVPI[220] VAc/VB[389] (NIPAM/**369**)[390]	 **214**[391]	VAc[391]

(*Continued*)

Table 10. (Continued)

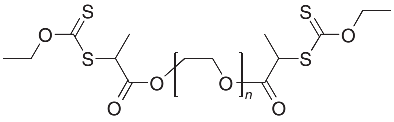
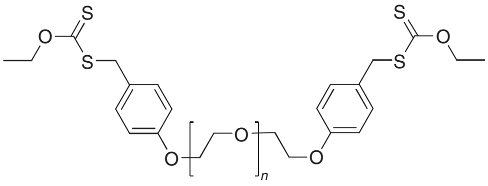
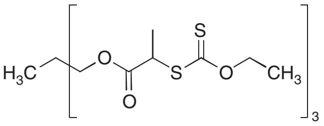
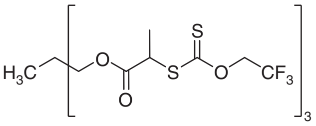
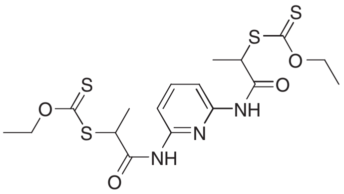
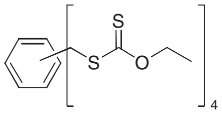
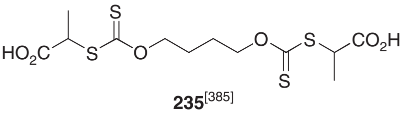
RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **215**	(AA)[60] BA/AA[279]	 **216***[283]	VAc[283]
 **217***[381]	(NVCL)[384] (NVPI)[220] NVP[381] **366**[380] **367**[380] **368**[380] NVP-*b*-VAc[381]	 **218**[392]	VAc[392]
 **219***	DADMAC[357]	 **220**[169]	VAc[169]
 **221**[393]	VAc[393]	 **222**[393]	*VAc*[393]
 **223***	(NVPI)[220]	 **224**[339]	–[C]
 **225**[339]	VAc[339] NVP[339]	 **226**[394]	(VAc)[394] NVP[394]
 **227**[395]	VAc[395]	 **228***	NVP[396]

[A] See footnote A of Table 3.

[B] See footnote B of Table 3.

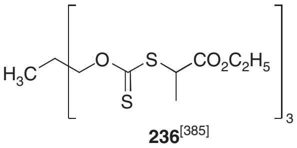
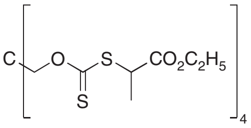
[C] Compounds not used as RAFT agents directly but served as precursors to other RAFT agents.

Table 11. Multi-RAFT agents and RAFT polymerizations – xanthate RAFT agents

RAFT agent[A]	Polymerizations[B]
‘R’-connected	
 PEO macro-RAFT agent **229**[394]	NVP[394]
 PEO macro-RAFT agent **230**[395]	VAc[395]
 **231***	AA[397]
 **232**[397]	AA[397]
 **233**[391]	VAc[391]
 **234** *ar*-1,2,4,5-substitution[381]	NVP[381]
‘Z’-connected	
 **235**[385]	VAc[385]

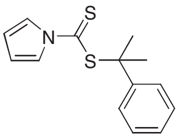
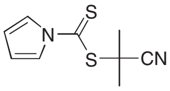
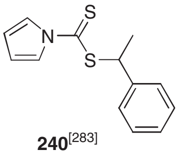
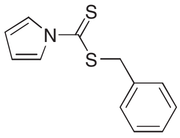
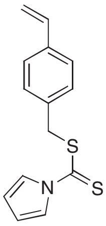
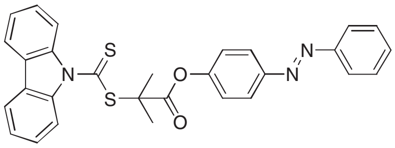
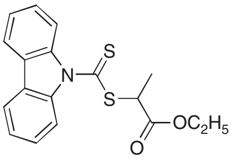
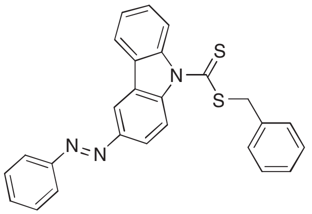
(*Continued*)

Table 11. (Continued)

RAFT agent[A]	Polymerizations[B]
‘Z’-connected	
 **236**[385]	VAc[385]
 **237**[385]	VAc[385]

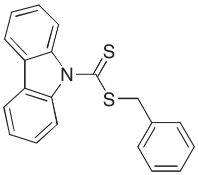
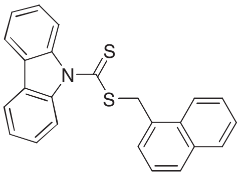
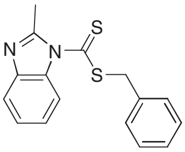
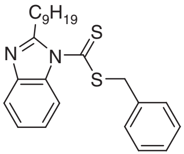
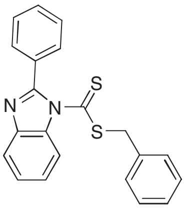
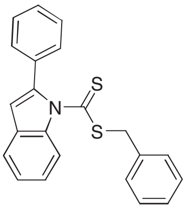
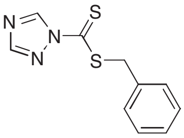
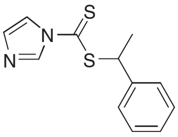
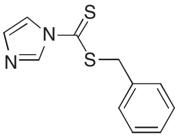
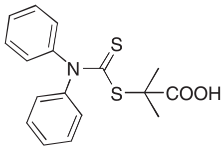
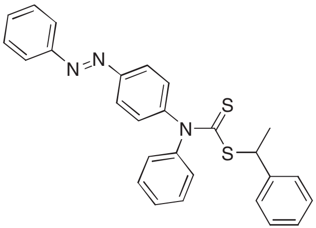
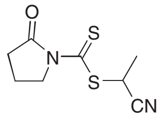
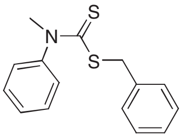
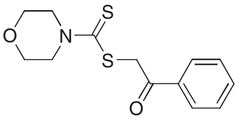
[A] See footnote A of Table 3.
[B] See footnote B of Table 3.

Table 12. RAFT agents and RAFT polymerizations – dithiocarbamate RAFT agents

RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **238***[398]	GMA[398] St[398] tBMA/DEGMA[398] tBMA/DEGMA-*b*-GMA[398]	 **239***	MMA[88]
 **240**[283]	St[73]	 **241***	MA[399] NIPAM[400] **331**[401] NVPI[220] **332**[221] **336**[221] **338**[221] NIPAM/**369**[390] (DMAM/**369**)[390] (MA/**369**)[390] St-*b*-**331**[401]
 **242**	NIPAM[229]	 **243**[402,403]	MMA[402,403]
 **244**[404,405]	MA[405] St[404]	 **245**[406]	MA[406]

(*Continued*)

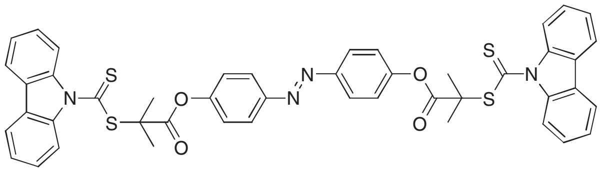
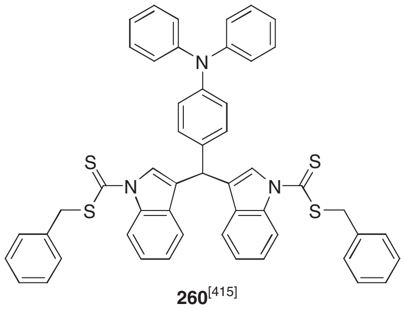
Table 12. (Continued)

RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **246***[406]	BA[406] MA[406] OA[406] St[406]	 **247**[405]	MA[405]
 **248**[405]	MA[405] St[407]	 **249**[408]	St[408]
 **250***[405]	MA[405] St[407,409]	 **251**[404]	MA[405] St[404]
 **252***	St[409]	 **253**[283]	
 **254***	**374**[410] MA/**374**[410] St/**374**[410]		(NVCL)[384]
 **255**[411]	MA[411] (St)[411]	 **256***	AA-*b*-NIPAM[412]
 **257**[283]		 **258**[413]	St[413] (MA)[413]

[A] See footnote A of Table 3.

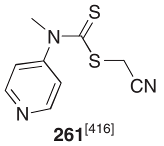
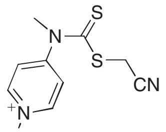
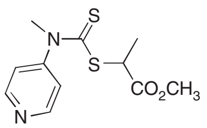
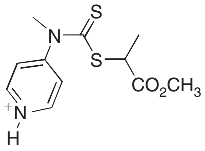
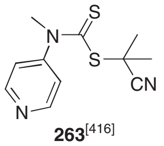
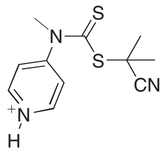
[B] See footnote B of Table 3.

Table 13. Multi-RAFT agents and RAFT polymerizations – dithiocarbamate RAFT agents

RAFT agent[A]	Polymerizations[B]
‘R’-connected	
 **259**[414]	St[414] St-*b*-MA[414] St-*b*-MA-*b*-NIPAM[414]
‘Z’-connected	
 **260**[415]	St[415]

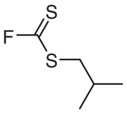
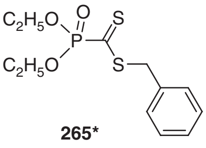
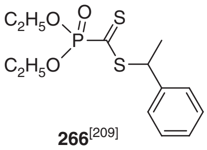
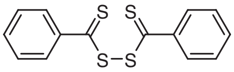
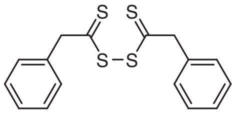
[A] See footnote A of Table 3.
[B] See footnote B of Table 3.

Table 14. RAFT agents and RAFT polymerizations – switchable dithiocarbamate RAFT agents

RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **261**[416]	(BA)[416] VAc[416]	 **261**-H$^+$[416]	BA[416]
 **262**[416]	NVP[416] NVC[416]	 **262**-H$^+$[416]	MA[416] St[416] (NVC)[416] MA-*b*-NVC[416][C]
 **263**[416]		 **263**-H$^+$[416]	MMA[416] MMA-*b*-VAc[416][C]

[A] See footnote A of Table 3.
[B] See footnote B of Table 3.
[C] RAFT agent was switched (neutralized) to make second block.

Table 15. RAFT agents and RAFT polymerizations – other RAFT agents[A]

RAFT agent[A]	Polymerizations[B]	RAFT agent[A]	Polymerizations[B]
 **264**[417]	(E)[417]		
 **265***	St[223,224,418]	 **266**[209]	St[419]
 **267***[34]	AN[420]	 **268***	AN[420] AN/MA[420] AN/MMA[420]

[A] See footnote A of Table 3.
[B] See footnote B of Table 3.

polymerization of methacrylates.[27] Dithiobenzoates **24** and **25** and the trithiocarbonates **121** and **125** are now commercially available from Strem Chemicals. RAFT agents are also available from Sigma-Aldrich and from Monomer-Polymer & Dajac Labs.[85]

Fig. 4, based on that from our previous reviews,[7–10] provides a general summary of how to select the appropriate RAFT agent for particular monomers. Note should be made of the dashed lines in the chart. Although some control might be achieved with these monomer RAFT agent combinations, the molecular weight distribution may be broad or there may be substantial retardation or prolonged inhibition. This proviso has been omitted in some representations of this data in the literature.

In synthesizing block copolymers by sequential monomer addition the order in which the blocks are prepared is important. The propagating radical derived from the macro-RAFT agent must be a reasonable free radical leaving group with respect to that formed by the monomer being polymerized.

RAFT agents such as dithioesters (Z = aryl or alkyl) or trithiocarbonates (Z = alkylthio) suitable for controlling polymerization of 'more-activated' monomers (MAMs), e.g., MMA, St, MA, acrylamide (AM), acrylonitrile (AN) inhibit or retard polymerizations of 'less activated' monomers (LAMs), e.g., VAc, NVP, and *N*-vinylcarbazole (NVC). Similarly RAFT agents suitable for controlling polymerizations of LAMs such as *N*,*N*-dialkyl- or *N*-alkyl-*N*-aryl dithiocarbamates and xanthates tend to be ineffective with MAMs.

The reduced effectiveness of the dithiocarbamate RAFT agents with MAMs relates to their lower reactivity towards radical addition and consequent lower transfer constants.[58] The double-bond character of the thiocarbonyl group is reduced by the contribution of zwitterionic canonical forms, which localize a positive charge on the nitrogen and a negative charge on the sulfur.[58,421] However, the tendency of dithioesters or trithiocarbonates to inhibit polymerization of LAMs is a consequence of the poor radical leaving group ability, with respect to the 'R' radical, of propagating species with a terminal LAM unit. Dithiocarbamates that possess electron-withdrawing groups adjacent to nitrogen or where the nitrogen lone pair is part of an aromatic ring system are effective with MAMs[58,421] but inhibit polymerizations of LAMs. Fluorodithioformates were proposed as universal RAFT agents but their application remains largely unproven.[417,422] One consequence of this has been that the direct synthesis of narrow dispersity polyMAM-*block*-polyLAM is difficult or not possible using the conventional range of conventional RAFT agents.

A new class of stimuli-responsive RAFT agents that can be switched to offer good control over polymerization of both MAMs and LAMs and a route to polyMAM-*block*-polyLAM has been reported.[416] *N*-(4-pyridinyl)-*N*-methyldithiocarbamates (Table 14) are effective with LAMs and in the presence of a strong acid, the protonated form of the *N*-(4-pyridinyl)-*N*-methyldithiocarbamates provide excellent control over the polymerization of MAMs.[416] The process is illustrated in Scheme 4 for the preparation of poly(methyl methacrylate)-*block*-PVAc. Thus in the first step the protonated RAFT agent (formed by adding 4-toluenesulfonic acid) is used to control the polymerization of MMA to form PMMA. This macro-RAFT agent is then neutralized in situ by adding a stoichiometric amount of *N*,*N*-dimethylaminopyridine (DMAP). RAFT polymerization of VAc then provided the desired block copolymer. Other approaches to the synthesis of polyMAM-*block*-polyLAM are mentioned in the section on Block Copolymers below.

It has also been reported that macro-RAFT agents derived from *N*,*N*-dialkylacrylamides are difficult to chain extend with *N*-alkylacrylamides.[302] Bivigou-Koumba et al.[286] reported that strong retardation was observed in extending PSt macro-RAFT agents with *N*-isopropylacrylamide (NIPAM), whereas chain extension of PNIPAM macro-RAFT with St was successful. In both cases slow initiation by the macro-RAFT agent-derived propagating species was suggested as a possible explanation. However, Wong et al.[218] reported that it was difficult to chain-extend PDMAM macro-RAFT agent with St and that it was important to make the PSt macro-RAFT agent first.

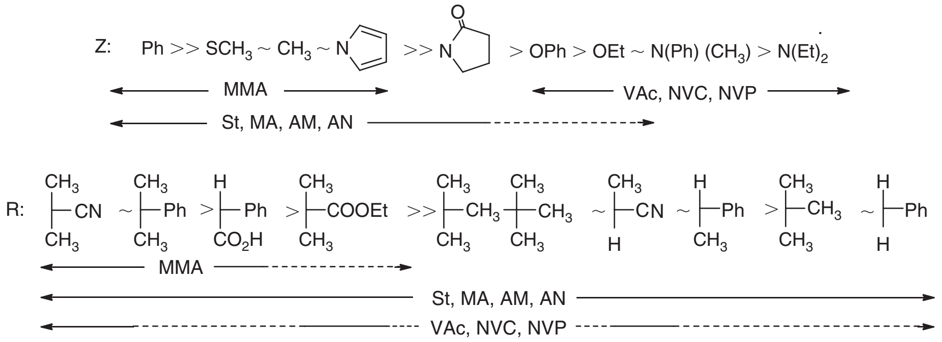
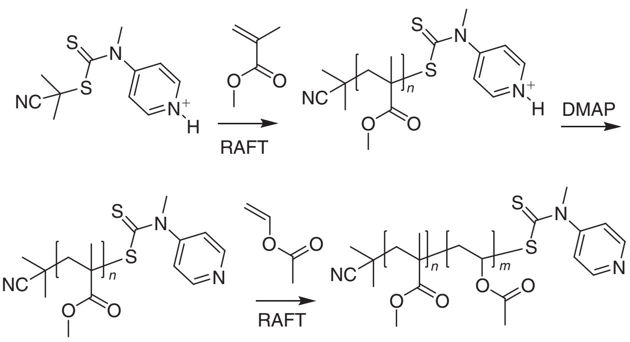
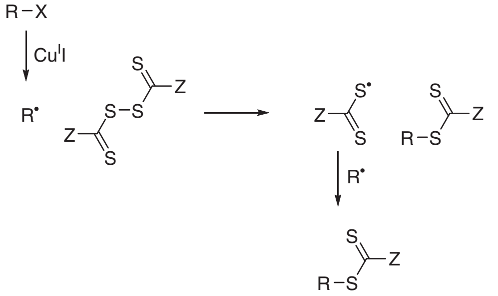


Fig. 4. Guidelines for selection of RAFT agents [Z–C(=S)S–R] for various polymerizations.[7] For Z, addition rates decrease and fragmentation rates increase from left to right. For R, fragmentation rates decrease from left to right. Dashed line indicates partial control (i.e., control of molecular weight but poor dispersity or substantial retardation in the case of VAc, NVC or NVP).



Scheme 4.



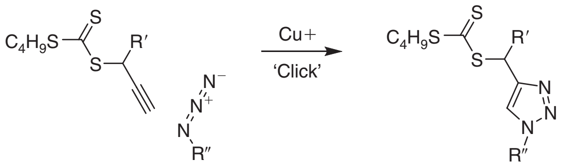
Scheme 5.

Synthesis of RAFT Agents

Primary and secondary trithiocarbonates, xanthates, and dithiocarbamate RAFT agents are commonly synthesized in high yield by reaction of the appropriate carbodithioate salt with an alkylating agent.[8,27,283] Skey and O'Reilly[283] advocated the use of acetone as solvent and phosphate as base and have applied the method to a wide range of RAFT agents (see Tables above). Surprisingly, in view of previous reports, they indicate that the method is also effective for the synthesis of some RAFT agents with tertiary 'R' (**115** and **143**).

Symmetrical trithiocarbonates are frequently synthesized from the corresponding halide, and carbon disulfide in the presence of a base. Aoyagi and Endo[290] have shown that this process can be performed on benzyl halides, and stoichiometric carbon disulfide at low temperature (40°C) in air with potassium bicarbonate as base to provide near quantitative yields of the corresponding dibenzyl trithiocarbonates (**111**–**114**).

RAFT agents can be synthesized from ATRP initiators as shown in Scheme 5. Dithioesters, dithiocarbamates, and xanthates were prepared in high yields by an atom transfer radical addition–fragmentation (ATRAF) process, using stoichiometric amounts of alkyl halides and bis(thiocarbonyl) disulfides in the presence of ATRP catalysts and, optionally, Cu metal as a reducing agent.[423] A similar procedure was described previously by Wager et al.[424]



Scheme 6.

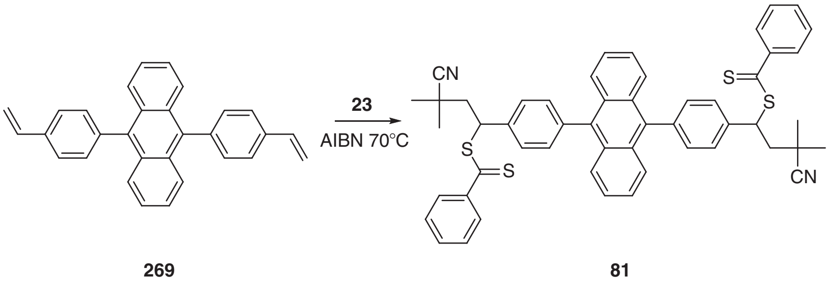
The synthesis of RAFT agents having a triazolinylmethyl leaving group are synthesized by a copper-catalyzed 3 + 2 cycloaddition reaction between an azide and a propargyl thiocarbonylthio compound (Scheme 6).[339] The triazolinyl trithiocarbonates **153** and **163** were effective in controlling polymerizations of St and BA, while the triazolinyl xanthate **225** was able to control polymerizations of NVP and VAc.

New RAFT agents can be synthesized by insertion of a single monomer unit into a RAFT agent.[425] The success of this process relies on the addition of R′ to the monomer being substantially faster than subsequent monomer additions and requires a very active RAFT agent such that the number of monomer additions per activation cycle is greater than 1. It requires selective initialization (see section on Mechanism of RAFT above). The methodology was applied in the synthesis of the bis-RAFT agent **81** (Scheme 7) which was used in the synthesis of light harvesting polymers.[244] Another recent example of this strategy is its application to 4-(*tert*-butoxy)styrene (tBS) to provide a route to mono-hydroxy end-functional PSt.[133]

The process has been adapted to provide a method for end-functionalizing macro-RAFT agents by addition of a single monomer unit to form a new macro-RAFT agent. Recent examples of this involve attachment of maleic anhydride (MAH) unit to a PSt macro-RAFT agent[186] and a single maleimide unit to a poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) macro-RAFT agent.[426]

Characterization of RAFT-Synthesized Polymers

Most papers on RAFT polymerization contain information on the characterization of RAFT-synthesized polymers and/or the RAFT process. We consider here papers where the



Scheme 7.

characterization of RAFT-synthesized polymers by spectroscopic or chromatographic methods is a primary focus.

A comparison of electrospray ionization (ESI) and matrix-assisted laser desorption–ionization time-of-flight (MALDI-TOF) mass spectrometries for characterizing PSt synthesized with dithiobenzoate **60** and AIBN initiation has been reported.[46] The relative merits of these techniques for characterizing PSt made by ATRP, NMP, and reverse iodine transfer polymerization (RITP) was also examined.[46] A MALDI-TOF mass spectrometry study of PSt with dithiobenzoate RAFT agents **69** and **70** has claimed to provide evidence of intermediate radical termination.[45] The application of ESI mass spectrometry to PSt with labile chain ends is facilitated by use of silver(I) tetrafluoroborate salt. The method was applied in identifying products and mapping reaction pathways in forming PSt with **92**,[254] PMA with **92**,[252] and PAA and PNIPAM with **103**,[269] and in forming star polymers from MA[268] and AcS[259] with **102**.

Dithiobenzoate RAFT agents and macro-RAFT agents were found to very effectively quench the fluorescence of coumarone derivatives and acenaphthalene units.[215,244,427] No quenching was observed for the RAFT-synthesized polymers from which the thiocarbonylthio end-group had been removed by aminolysis[215] or radical-induced reduction.[244]

On-line monitoring of RAFT polymerization by NMR and other methods is mentioned above in the section Mechanism of RAFT.

RAFT synthesized polymers, in particular PSt or PMMA with dithiobenzoate chain ends, have been found to be unstable to storage in cyclic ether solvents (tetrahydrofuran).[428] Thus PMMA-dithiobenzoate was converted into PMMA-hydroperoxide within 7 days. PSt-dithiobenzoate was more slowly converted into a mixture of products in which the dithiobenzoate end-group had been converted into the corresponding sulfine or thionoester end-groups or was lost and the polymer left with epoxy and unsaturated end-groups. The end-group degradation was attributed to the presence of tetrahydrofuran hydroperoxide in the solution. Much slower degradation was also observed in dichloromethane solution. The result has implications with respect to storage of samples for gel permeation chromatography where tetrahydrofuran is commonly used as solvent/eluent. We have also observed that RAFT-synthesized polymers (not just dithiobenzoates) can be unstable in tetrahydrofuran solution and recommend that only peroxide-free solvent is used and that samples, if they must be kept, are stored under an inert atmosphere and protected from light.

Polymerization Kinetics

Kinetic simulation is frequently used as a tool to correlate experimental data with theoretical models.[429] The use of RAFT polymerization and kinetic simulation with Predici have been applied to determine chain length dependent termination rate constants in radical polymerizations (the RAFT-CLD-T method) has been previously reviewed.[19]

Criteria for selecting conditions for the determination of termination rate constants by the RAFT-CLD-T method have been proposed and justified by kinetic simulation.[430] The RAFT-CLD-T method has been used to determine chain length dependent termination rate constants in MMA polymerization in various conversion regimes up to high conversion[119,120] and termination rate constants during formation of star polymers based on MMA, MA, and St.[20,256]

In the SP-PLP-NIR-RAFT method, polymerization is induced by a single laser pulse (SP) and the resulting decay in monomer concentration, c_M, is monitored by NIR spectroscopy with a time resolution of microseconds. The presence of a RAFT agent ensures the correlation of radical chain length and monomer-to-polymer conversion.[281,429] The method has been applied to determine chain length dependent k_t in MA,[281] BA,[429] and DA[281] polymerizations.

A kinetic simulation was used to model RAFT polymerization controlled by bis-RAFT agents.[431] It was demonstrated theoretically that the use of such RAFT agents allows production of linear polymers with an extremely low level of dead chains. This is a consequence of it being statistically unlikely to produce chains with zero RAFT end-groups.

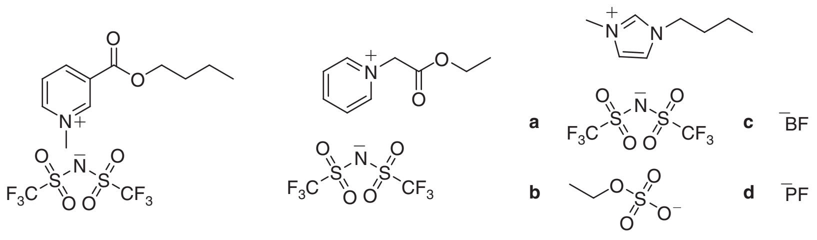
Reaction Conditions (Initiator, Temperature, Pressure, Solvent, Lewis Acids)

The general guideline for choosing initiator concentrations for RAFT polymerization is that the mole ratio of RAFT agent to amount of initiator decomposed should be $>10:1$ and be such that the molecular weight obtained in a control experiment (i.e., same conditions without RAFT agent) is at least 10-fold higher than the desired molecular weight.[7] It must be remembered that for every pair of radicals generated, a pair of radicals will terminate to provide dead polymer impurity.

RAFT polymerizations with either **24** or **254** as RAFT agent were successfully carried out at room temperature using benzoyl peroxide/*N*,*N*-dimethylaniline as a redox initiator.[410]

A detailed study of the RAFT polymerization of MA with a trithiocarbonate RAFT agent (**157**) and AIBN initiator at 50°C has appeared.[344] The variables explored were: ratio of RAFT agent to initiator (1:5 to 1:0.1), ratio of RAFT agent to monomer (500:1 and 100:1), monomer concentration (bulk and 33.3 wt-% monomer in solvent) and solvent (toluene, DMF, MEK). For this system, good control was achieved under all conditions studied.

Several papers have appeared on the protocol for conducting high-throughput RAFT polymerization.[114,115,251] High throughput methods have been applied to synthesize libraries



270 **271** **272**

Fig. 5. Structures of ionic liquids.

of methacrylate polymers (MAA, various oligo(ethylene glycol) methacrylates and copolymers of MAA with PEGMA,[108] MMA, DMAEMA and block and statistical copolymers,[114] and copolymers of DMAEMA with PEGMA[113]) for evaluating the composition dependence of the lower critical solution temperature (LCST).

RAFT polymerization of 'polar' monomers (MMA,[432] MA,[432,433] VAc,[433] DADMAC,[434] and NIPAM[304]) were reported to be substantially accelerated by microwave heating. Less but still significant acceleration was observed for St polymerization.[432,433,435] It is expected that monomers with a higher dielectric constant will be more effectively heated by microwave irradiation. The microwave effect, particularly with MMA and MA, was suggested to be greater than expected for an effect of temperature alone,[432] although an alternate explanation has not yet been provided. A more recent study on MMA polymerization[109] indicates that the polymerization kinetics are independent of whether microwave or conventional heating processes are used. The advantage of a microwave reactor is that it allows RAFT polymerization to be readily conducted at high temperatures in superheated monomer. Thus, RAFT polymerizations of MMA were carried out at 120, 150, and 180°C in the absence of an added radical initiator.

Several studies on photo-initiated RAFT polymerization have appeared.[270,275,285,309,413,436] RAFT polymerization of St derivatives can be carried out at near ambient temperature (30°C) with **115** as RAFT agent using 365 nm irradiation and (2,4,6-trimethylbenzoyl)-diphenylphosphine oxide as photoinitiator.[309] The same photoinitiator with 420 nm irradiation was used in ambient temperature RAFT polymerization of the UV sensitive cinnamate derivative **298**[436] and for polymerization of BA and MA under solar irradiation (>400 nm) at 20°C.[270]

The use of ionizing radiation to initiate RAFT polymerization has been reviewed.[33,437] Other studies on gamma-initiated RAFT polymerization include the polymerization of MA and BA,[252] polymerization of NIPAM[269] and AA[269,354] in aqueous media, BA miniemulsion polymerization,[253] St/MAH/NVP terpolymerization,[288,289] MA polymerization with dithiocarbamate RAFT agents[405] and the grafting of styrenic monomers to cellulose[167,438] and *t*-butyl acrylate onto ethylene propylene rubber.[439]

Further experiments have been reported on RAFT polymerization in the presence of a Lewis acid to control tacticity (**110**/AM/Y(OTf)$_3$;[285] **94**/NIPAM/Sc(OTf)$_3$;[262] **94**/NIPAM/Y(OTf)$_3$;[262] **103**/NIPAM/Y(OTf)$_3$;[271] and **119**/MMA/Sc(OTf)$_3$[88]). The disappearance of the RAFT agents (cumyl dithiobenzoate **22** or cyanoisopropyl dithiobenzoate **24**) in solution at 60°C in the presence of a Lewis acid (Sc(OTf)$_3$) was followed by NMR spectroscopy.[88] These RAFT agents underwent significant decomposition within 1 h and were completely converted into a complex mixture of products within 16 h. RAFT agent instability provides an explanation for the poor control over molecular weight distribution observed in earlier attempts to achieve control over tacticity of PMMA.[88] Other RAFT agents, including dithiobenzoate **39**, cyanoisopropyl methyl trithiocarbonate **119**, and cyanoisopropyl 1-pyrrolecarbodithioate **239**, and the PMMA macro-RAFT agents formed with use of these RAFT agents were found to be stable in the presence of Lewis acid over a 16 h period at 60°C.[88] RAFT polymerization of MMA in the presence of **119** and Sc(OTf)$_3$ provided simultaneous RAFT-controlled molecular weight and molecular weight distribution ($Đ < 1.3$ at >95% conversion), Lewis acid-controlled tacticity with $mm{:}mr{:}rr = 12{:}44{:}44$ for a mole ratio Sc(OTf)$_3$/MMA of 1:8.5 at 60°C [compared with $mm{:}mr{:}rr = 4{:}33{:}63$ in the absence of Sc(OTf)$_3$] and a significantly enhanced rate of polymerization.[88] The effect of the Lewis acid on tacticity was the same as that observed in the absence of RAFT agent.

The rate of RAFT polymerization of MA with **241** is substantially enhanced in the presence of alumina, which is attributed to the alumina acting as a Lewis acid.[399]

RAFT polymerization of St was successfully carried out in biodegradable ionic liquids **270** or **271** (RAFT agent **92**, 90°C, ACHN initiator) (Fig. 5).[255] The polymerization kinetics were similar to those for toluene solution. Note that previous attempts to polymerize St in conventional imidazolium ionic liquids were unsuccessful. The outcome of RAFT polymerization of MMA with **24** or **115** in imidazolium ionic liquids (**272a**–**d**) is dependent on the counteranion with best results being obtained with **272a** and **272d** and relatively poor control being seen with **272b** or **272c** as solvent.[122]

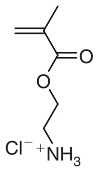
RAFT polymerization of cyclodextrin host–guest complexes has been performed. Precipitation was observed during RAFT-polymerization of the cyclodextrin host–guest complex of styrene.[356] However, homopolymerization of a cyclodextrin host–guest complex of the adamantyl derivative **346** remained homogeneous allowing synthesis of the amphiphilic block copolymers P**346**-*block*-PDMAM in aqueous solution.[358]

RAFT Polymerization in Heterogeneous Media

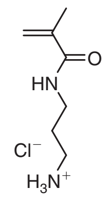
Several reviews relating to the use of RAFT in heterogeneous media have appeared.[29,440–442] Examples of RAFT polymerizations in heterogeneous media are included in Tables 3–15 and are distinguished in the tables by the monomer appearing in italics.

The use of macro-RAFT agents as stabilizers in 'surfactantless' emulsion polymerization,[145,181,225,287,300,310,341,393,443–446] miniemulsion polymerization,[124,181] suspension polymerization[381] and non-aqueous dispersion polymerization in both organic media,[188] and in supercritical CO$_2$[353,389,447,448]

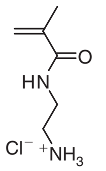
Table 16. Ammonium functional monomers subjected to RAFT polymerization



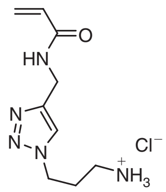
AEMA
273[90,451]



APMAM
274[152,153,168]



AEMAM
275[153]



276[166]

has gained popularity. Particle nucleation and growth during RAFT emulsion polymerization of St and BA mediated by macro-RAFT agents of various compositions has been studied by calorimetry.[341] More hydrophilic amphipathic macro-RAFT agents (e.g., AA 10 units–St 10 units) were thought to be promising for producing latex products with best control over particle number and particle size distribution. In most cases this work has involved use of a hydrophilic or an amphiphilic macro-RAFT agent. However, macro-RAFT agents based on dextran[393] or poly(ethylene oxide) (PEO)[124,181,444] have also been exploited.

There have been several papers on the use of the RAFT process in the dispersion polymerization of St,[353] MMA,[447,448] and NVP[389] in supercritical CO_2 making use of macro-RAFT agents as stabilizer.

Kinetic simulation of the RAFT miniemulsion polymerization was performed to investigate the polymerization rate[449] and molecular weight distribution.[450] It was found that the polymerization rate increases with a reduction in the particle size. However, for particles with particle diameter (D_p) < 100 nm, the statistical variation in monomer concentration among the particles should not be neglected and may slow the polymerization rate.[449] The variation in monomer concentration between particles may also cause a broadening of the molecular weight distribution by causing different molecular weights of polymer to be formed.[450]

RAFT Polymer Syntheses

Polymer syntheses by RAFT polymerization are summarized in Tables 3–15. Only systems that require separate comment are mentioned here or in subsequent sections.

RAFT technology is generally incompatible with unprotected primary or secondary amine functionality. Recently, several groups have reported that the polymerization of monomers with primary amine functionality (**273**–**276**) (Table 16) can be effectively controlled with the monomer as the ammonium salt and with no or minimal loss of the RAFT end-group.[90,152,153,166] Some of the more exotic monomer subjected to RAFT polymerization are included in the tables that follow. They include methacrylates (Table 17), acrylates (Table 18), methacrylamides (Table 19), acrylamides derived from amino acids (Table 20), other acrylamides (Table 21), St derivatives (Table 22), and vinyl monomers (Table 23). Monomers of the above classes with reactive functionality are in Tables 14–26. Macromonomers are considered in the section Polymer Brushes/Graft Copolymers/Comb Polymers/Surface Modification.

Other functional monomers to receive attention include fluorinated methacrylates (**280**–**281**, PFMA, TFPMA), acrylates (**318**, TFPA), and styrenes (PFS), monomers with betaine (**292**–**293**), thiirane (**301**), boronic acid (**343**), and pyridyl disulfide (**391**) and a wide range of other functionalities. The number of examples of synthesis of glycopolymers using RAFT polymerization has substantially expanded. These have been prepared by the polymerization of methacrylate **285**–**291**, acrylate **319**, St **356**, acrylamide **342**–**340**, or methacrylamide **325**–**326** glycomonomers. There has also been significant interest in RAFT polymerization of acrylamides derived from amino acids (**330**–**339**; Table 20).

Use of 'click chemistry' in polymer chemistry has recently attracted much attention.[461–464] The clickable functionality may be present in the monomers or on the Z or R groups of the RAFT agent (see Block Copolymers). The clickable monomers are incorporated as homopolymer blocks as a precursor to a polymer brush, or copolymerized to provide sites for attachment of functionality or for crosslinking.

A significant number of these papers concern the combination of RAFT and azide–alkyne 1,3-dipolar cycloaddition. Azide- and alkyne-functional monomers are given in Table 24. The importance of protecting alkyne-functional monomers (**371**, **373**) (and RAFT agents) as the trimethylsilyl derivative has been stressed by some authors. However, some have been used unprotected with apparently minimal side reactions, which is attributed to the alkyne being much less reactive towards radical addition than the (meth)acrylate double bond. Azide-functional polymers have also been prepared from 3-chloropropyl acrylate polymers, which are converted to 3-azidopropyl acrylate copolymer post polymerization by reaction with sodium azide.[338,346]

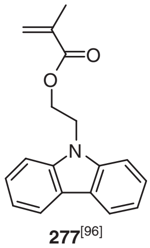
'Active ester' monomers that have been subject to RAFT polymerization are **379**–**386** shown in Table 25.[465] These active ester groups undergo facile reaction with, in particular, substrates with primary amine groups. Other monomers with reactive functionality that have been successfully (co)polymerized include **391** (with thiol reactive functionality)[161,162] and **392** (with protected aldehyde functionality) (Table 26).[97,98]

Copolymers of monomers with reactive functionality, such as **371**–**392** (Tables 24–26), have potential application as scaffolds for bioconjugation. This and other applications are considered below in the section Polymer Brushes/Graft Copolymers/Comb Polymers/Surface Modification.

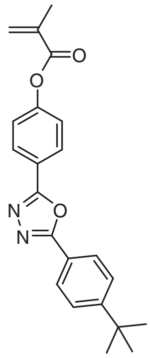
End-Functional Polymers and End-Group Transformations

Processes for thiocarbonylthio end-group removal or transformation post RAFT polymerization continue to attract significant interest.

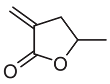
Table 17. Methacrylate monomers subjected to RAFT polymerization



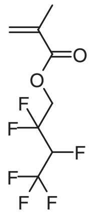
277[96]



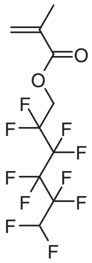
278[96]



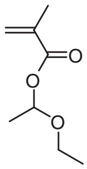
MMBL
279[258]



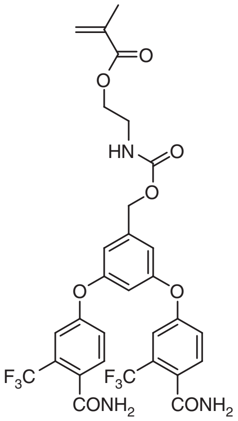
280[124,145]



281[124]



282[110]



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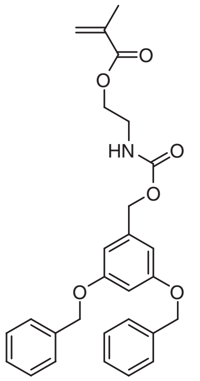

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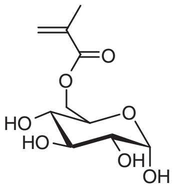
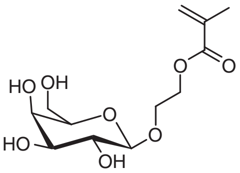


285[156]



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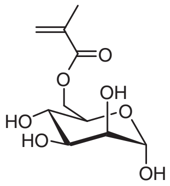
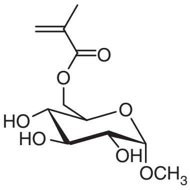


287[170]



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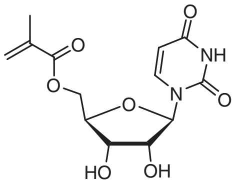

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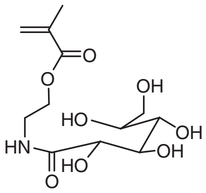

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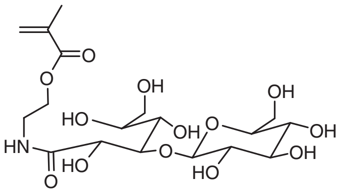
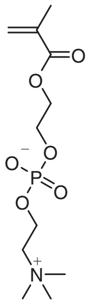
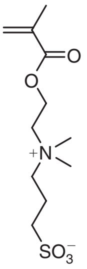


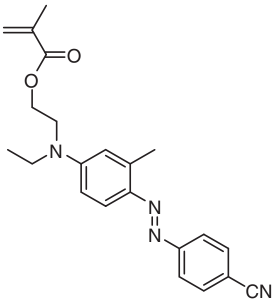
291[453]



MPC
292[139,158]



DMAPS
293[158]



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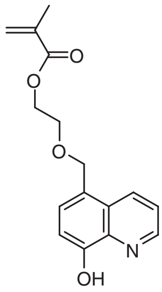

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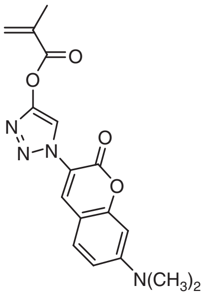
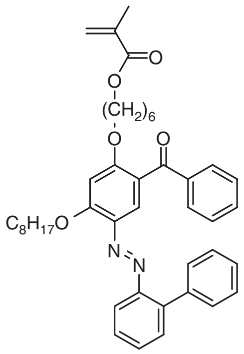


296[127]

(*Continued*)

Table 17. (Continued)



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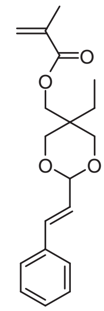

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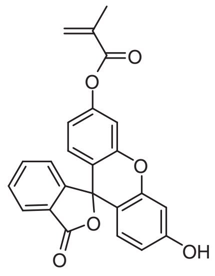

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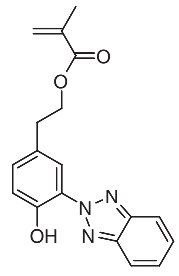

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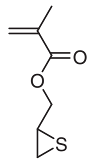

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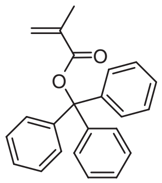
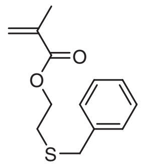


TPMMA
302[92]



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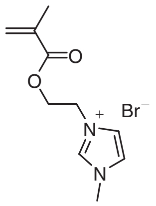

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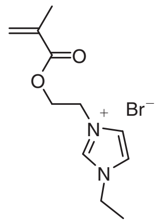

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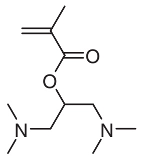

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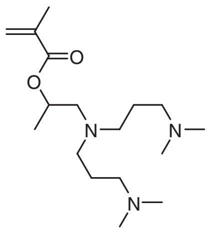

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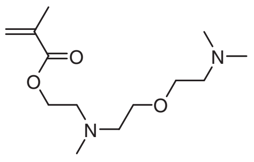

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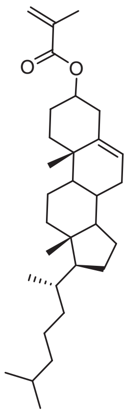
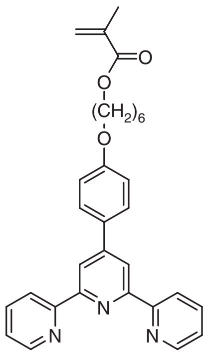


CMA
309[295,301]



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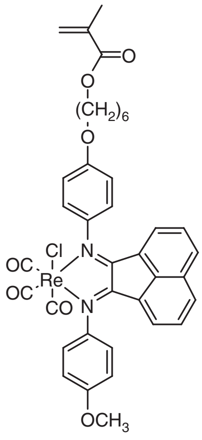

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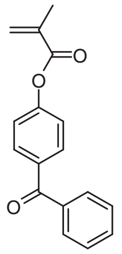
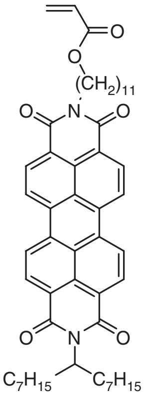


312[210]

Table 18. Acrylate monomers subjected to RAFT polymerization



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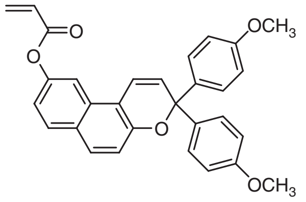

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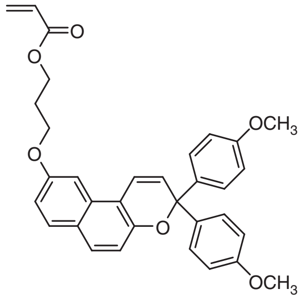

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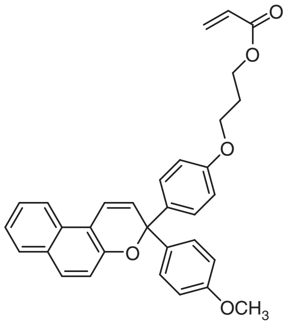
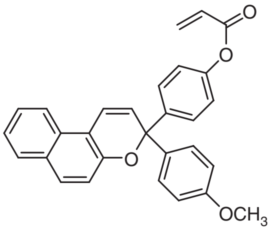
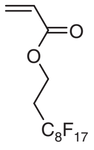


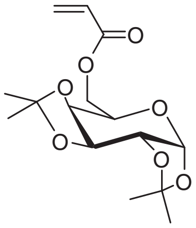
316[137]



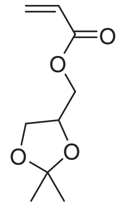
317[137]



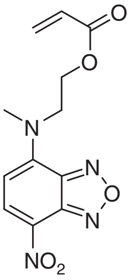
318[308]



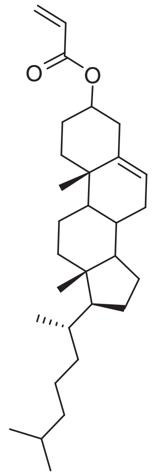
319[352]



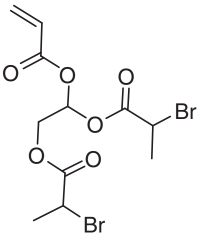
320[165]



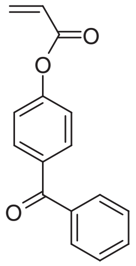
321[374]



CA
322[297]

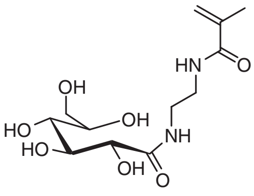


323[185]

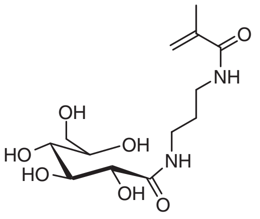


324[210]

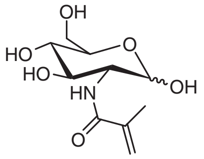
Table 19. Methacrylamide derivatives subjected to RAFT polymerization



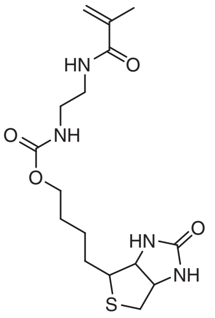
325[154]



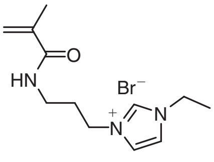
326[154]



327[157]

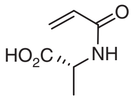


328[278]

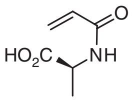


329[140]

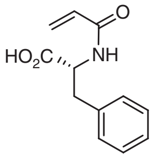
Table 20. Amino acid-derived acrylamides subjected to RAFT polymerization



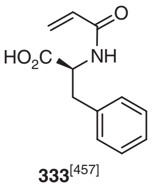
(*R*)-2-acrylamidopropanoic acid
330[318,457]



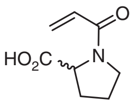
(*S*)-2-acrylamidopropanoic acid
331[159,318,401,457]



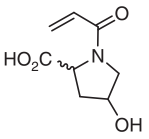
332[221,457]



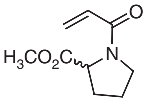
333[457]



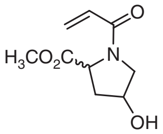
334[458]



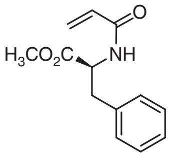
335[458]



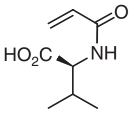
336[221,458]



337[458]

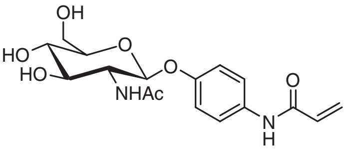


338[221,235,401,457]

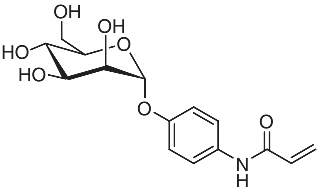


339[319]

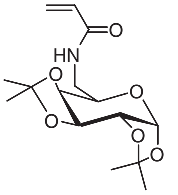
Table 21. Acrylamide derivatives subjected to RAFT polymerization



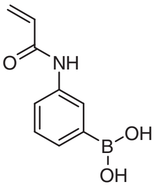
340[239]



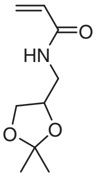
341[239]



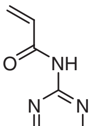
342[212,278]



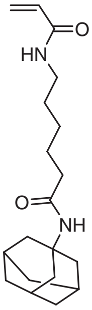
343[312]



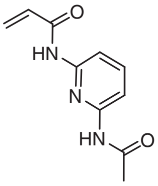
344[165]



345[99]

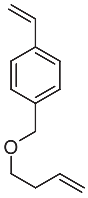


346[358]

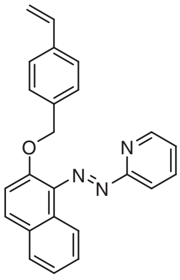


347[101]

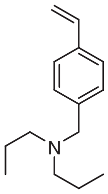
Table 22. Styrene derivatives subjected to RAFT polymerization



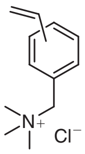
348[100,199]



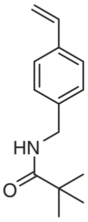
349[138]



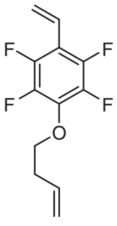
350[158,309]



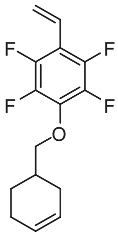
VBTAC
351[159]



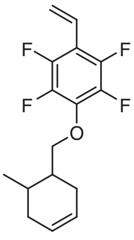
352[459]



353[321]



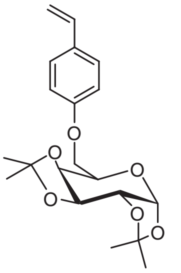
354[313]



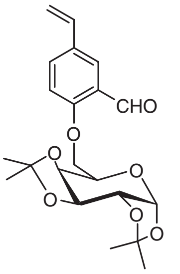
355[313]

(*Continued*)

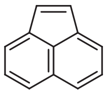
Table 22. (Continued)



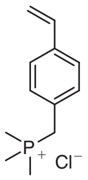
356[460]



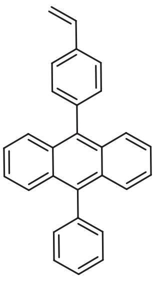
357[206]



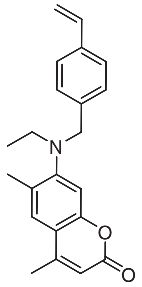
358[244]



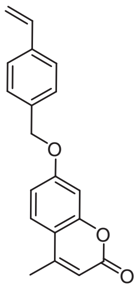
VBTPC
359[34]



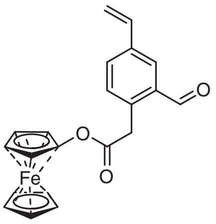
360[244]



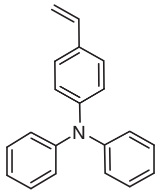
361[250]



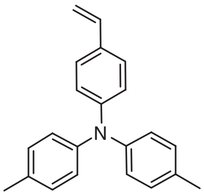
362[207]



363[134]

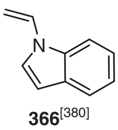


364[102]

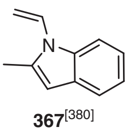


365[102]

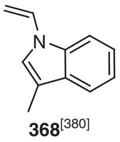
Table 23. Vinyl derivatives subjected to RAFT polymerization



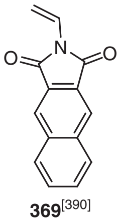
366[380]



367[380]

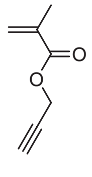


368[380]

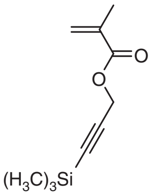


369[390]

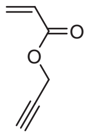
Table 24. Alkyne and azide clickable monomers amenable to RAFT (co)polymerization



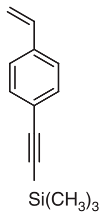
370[135,146]



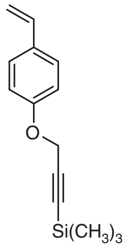
371[111,135]



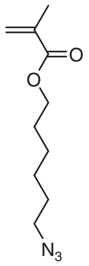
372[338,346,347]



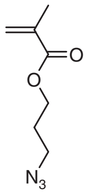
373[201]



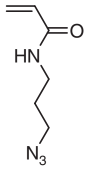
374[459]



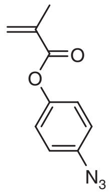
375[136]



376[195]

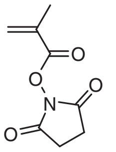


377[150]

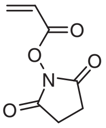


378[410]

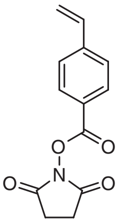
Table 25. Active ester monomers amenable to RAFT (co)polymerization



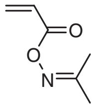
MAS
379[466]



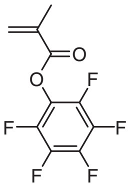
NAS
380[160,299,317,345,347]



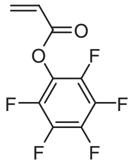
381[178]



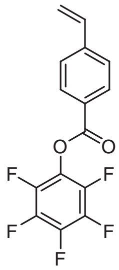
382[222]



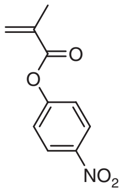
383[149,467]



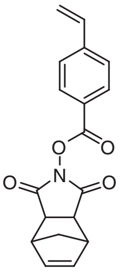
384[102,141,155]



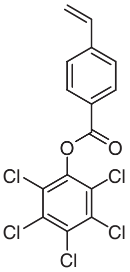
385[104,468]



386[97,98]



387[104]



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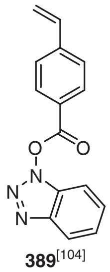

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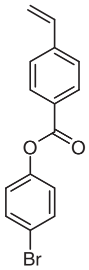


390[104]

Radical-Induced Reduction

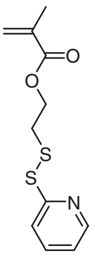
Several new papers have appeared on radical-induced reduction that allows the thiocarbonylthio group of a RAFT-synthesized polymer to be replaced with a hydrogen atom.[94,244,395,469] It was found that the end-groups of the (meth)acrylic polymers, e.g., PBA and PMMA were more readily reduced than those of PSt and the efficiency of hydrogen atom donors increases in the series toluene < propan-2-ol < triethylsilane < triphenylsilane ∼ tris(trimethylsilyl)silane ∼ *N*-ethylpiperidine hypophosphite < tri-*n*-butylstannane.[94] The use of hypophosphite salts, in particular, *N*-ethylpiperidine hypophosphite, overcomes reagent toxicity and workup issues associated with the use of stannane and silane H-donors. For organic-soluble polymers workup is simplified to a water wash. Radical-induced reduction with tri-*n*-butylstannane was used to remove xanthate chain ends from PVAc (Table 27).[395]

Addition–Fragmentation Coupling

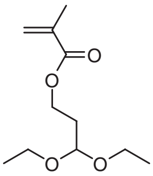
Another popular method for end-group removal/transformation involves heating the RAFT-synthesized polymer with a large excess of a radical initiator, most often an azo compound.[470,471] Recent examples include removal of dithioester or trithiocarbonate end-groups from polymers with a terminal methacrylate, acrylate, methacrylamide, acrylamide unit, or styrene (Table 28).

It was reported that bimodal distributions are obtained with a MA polymer when temperatures higher than 80°C were used.[164] The problem was attributed to the higher radical flux that results at higher temperatures. We found that with this method, while successful for removing the chain ends of polymers with a terminal MA unit, it was not possible to obtain complete removal of dithiobenzoate or butyl trithiocarbonate ends from polymers with a terminal BA[472] or St unit,[472,473] even when using a very large molar excess (up to 100-fold) of initiator (AIBN) and extended reaction times. The method was not effective for removing xanthate chain ends from PVAc.[395] The issues with incomplete end-group removal are most likely associated with the cyanoisopropyl radical (a very good radical leaving group) not being effective in displacing the propagating species.

Table 26. Monomers with masked reactive functionality amenable to RAFT (co)polymerization



391[161,162]



392[97,98]

A further cautionary note when using this method to introduce functionality by end-group transformation, is that the reaction of (for example) cyanoisopropyl radicals with propagating radicals may involve disproportionation as well as the intended combination. For example, the combination/disproportionation ratio (k_{td}/k_{tc}) for cyanoisopropyl reacting with PSt propagating radical is 0.61.[1]

The use of peroxide initiators (didodecyl peroxide, dibenzoyl peroxide) in end-group removal has also been explored in the context of using such initiators in radical-induced reduction.[94] These initiators appear generally more effective than azo initiators, for example, AIBN, in achieving end-group removal. However, the complication of termination by self reaction of propagating species is much more pronounced.[94]

Thermolysis

The thermal stability of RAFT-synthesized PMMA has been studied by several groups.[116,121] PMMA with a methyl trithiocarbonate end-group undergoes loss of that end-group at ∼180°C, at least in part, by homolysis of the C–CS_2SCH_3 bond and subsequent depropagation.[121] In contrast, PMMA with a dithiobenzoate end appears more stable. Only the end-group is lost at ∼180°C and the dominant mechanism is proposed to be a concerted elimination process analogous to that involved in the Chugaev reaction (Scheme 8).[121]

Thermal elimination of the end-groups from PSt or PBA with secondary xanthate end-groups occurs at relatively low temperatures. It is proposed that the elimination proceeds selectively to produce a polymer with a thiol chain end also by a Chugaev mechanism (Scheme 9).[469] In contrast butyl trithiocarbonate end-groups are cleaved from RAFT-synthesized PSt[473,477] and PBA[477,478] at relatively high temperatures with elimination of a thiol and formation of an unsaturated end-group.

Aminolysis/Hydrolysis/Ionic Reduction

A summary of the use of aminolysis or ionic reduction (typically use of borohydride) is provided in Table 29. It was reported that aminolysis of PNIPAM trithiocarbonate proceeds quantitatively to the thiol when conducted in the presence of a

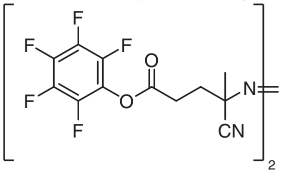
Table 27. Examples of end-group removal by radical-induced reduction

Terminal monomer unit[A]	Z (initial RAFT agent)	H donor[B]	Ref.
St	$C_{12}H_{25}S$ (**159**)	$((CH_3)_3Si)_3SiH$	[94]
St	$C_{12}H_{25}S$ (**159**)	EPHP	[94]
BA	$C_{12}H_{25}S$ (**159**)	EPHP	[94]
tBA	$C_{12}H_{25}S$ (**135**)	EPHP	[328]
MMA	$C_{12}H_{25}S$ (**121**)	EPHP	[94]
St	Ph (**22**)	EPHP	[94]
358	Ph (**22**)	Bu_3SnH	[244]
VAc	C_2H_5O (**227**)	Bu_3SnH	[395]

[A] Monomer unit adjacent to thiocarbonylthio group.

[B] $((CH_3)_3Si)_3SiH$ – tris(trimethylsilyl)silane, EPHP – *N*-ethylpiperidine hypophosphite, Bu_3SnH – tri-*n*-butylstannane.

Table 28. Examples of end-group removal by addition–fragmentation coupling



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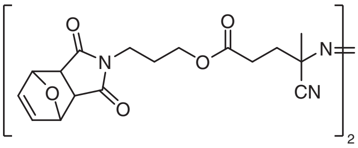

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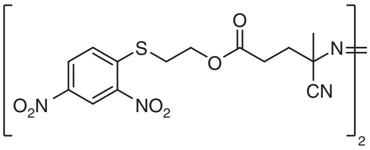

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Terminal monomer unit[A]	Z (initial RAFT agent)	Initiator	Ref.
HEA	$C_{12}H_{25}S$ (**187**)	AIBN	[370]
MMA	Ph (**28**)	AIBN	[173]
MMA	Ph (**28**)	**393**	[173]
MMA	$C_{10}H_7$ (**42**)	AIBN[B]	[194]
416	Ph (**25**)	ACVA[C]	[164,474]
DMAPMAM	Ph (**25**)	AIBN	[168]
NIPAM	C_2H_5S (**185**)	**394**	[368]
NIPAM	C_2H_5S (**189**)	**394**	[374]
NIPAM	$C_{12}H_{25}S$ (**139**)	AIBN	[324]
NIPAM	S(PDMAM-*b*-PNIPAM) (**398**)	AIBN	[475]
DMAM	S(PDMAM) (**398**)	AIBN	[475]
NAM/NAS	$C_{12}H_{25}S$ (**115**)	AIBN	[299]
St	Ph (**24**)	AIBN	[133]
St	C_4H_9S (**160**)	AIBN[D]	[473]
St	Ph (**50**)	**395**	[476]
St	S(PSt) (**398**)	AIBN	[475]
VAc	C_2H_5O (**230**)	AIBN[E]	[395]

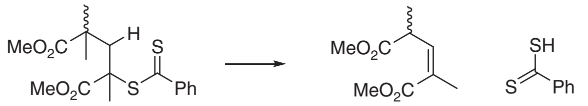
[A] Monomer unit adjacent to thiocarbonylthio group.

[B] In supercritical CO_2.

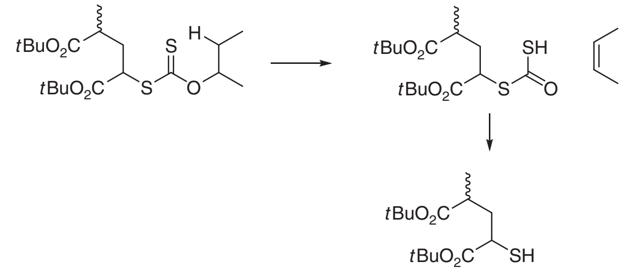
[C] Bimodal distribution observed for higher reaction temperatures (>80°C).

[D] Incomplete end-group removal.

[E] End-group not removed.



Scheme 8.



Scheme 9.

small amount of a phosphine reducing agent (TCEP).[371,372] Two groups have compared aminolysis with borohydride reduction for PSt dithiobenzoate.[117,205] One study[205] compared (a) sodium borohydride in aqueous THF, (b) sodium borohydride in toluene with phase transfer catalysis, (c) lithium triethylborohydride in THF, and (d) propylamine in THF. The reaction (a) with sodium borohydride in aqueous THF was slow yet yielded the cleanest product. Aminolysis with propylamine (d) gave a substantial yield of the disulfide. The other reductions (b) and (c) gave, in addition, other unidentified byproducts. In the second study it was reported that disulfide formation during borohydride reduction or during was a problem even in the presence of a phosphine, $P(Bu)_3$.[117]

Several groups have found that disulfide formation can be prevented if the thiol formed can be allowed to react in situ.[117,130,373,479,480] For example, end-group reduction can be performed in the presence of a Michael acceptor (to do an in-situ thiol-ene reaction).[117,130,479] This methodology has been applied to the synthesis of three-armed stars by an in-situ thiol-ene reaction with a triacrylate[130] and has been applied to directly make biopolymer conjugates.[479]

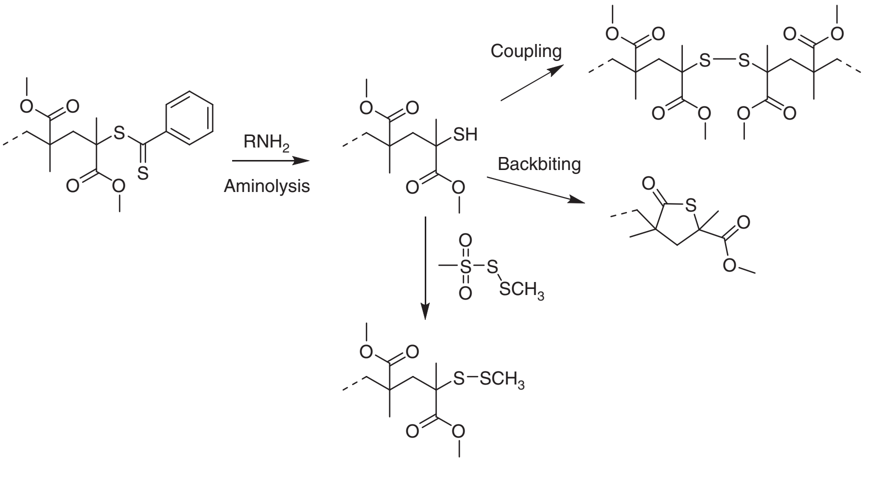
A recent study shows that dithioester and trithiocarbonate RAFT agents [R–SC(S)Z] undergo a radical-catalyzed reaction with thiols that results in oxidation of the thiol to a disulfide and concomitant reduction of the RAFT agent to R–H.[481] The relative rates of reaction suggested that dithioester RAFT agents

Table 29. Examples of conversion thiocarbonylthio end-groups to thiol end-groups by reaction with nucleophiles

Terminal monomer unit[A]	Z (initial RAFT agent)	Reagent	Comment	Ref.
PEGA	Ph (**49**)	Butylamine	Used in thiol-ene	[204]
PEGA	Ph (**58**)	Butylamine	Used in thiol-ene	[204]
NIPAM	$SCH_2CH(CH_3)_2$ (**188**)	Butylamine/TCEP/HEA butylamine/TCEP/BA	One-pot thiol-ene	[373]
NIPAM	$SCH_2CH(CH_3)_2$ (**188**)	Butylamine/TCEP	Used in thiol-ene	[371,372]
NIPAM	Ph (**25**)	$LiB(C_2H_5)_3H$	Used in thiol-ene	[151]
NIPAM	$S(CH_2)_2CO_2H$ (**170**)	$NaBH_4$	Used in thiol-ene	[355]
NIPAM	SC_4H_9 (**166**)	NaOH/MeOH/EDTA	Used in thiol-ene	[412]
NIPAM	Ph (**24**)	Octylamine/DMPP/AMA	One-pot thiol-ene	[132]
NIPAM	Ph (**24**)	Octylamine/DMPP/PMA	One-pot thiol-ene	[132]
DEAM	Ph (**24**)	Hexylamine/DMPP/MA	One-pot thiol-ene	[130]
St	Ph (**24**)	Propylamine/PBu_3/MA $NaBH_4$/PBu_3/MA	One-pot thiol-ene	[117]
St	Ph (**24**)	Propylamine $NaBH_4$		[205]
MMA	Ph (**82**)	Hexylamine	Conditions to favour disulfide formation	[196]
MMA	Ph (**22**)	Propylamine	One-pot methanethiosulfonate	[480]
NVP	OC_2H_5 (**228**)	$NaBH_4$	Used in peptide/nucleotide conjugation	[396]

[A] Monomer unit adjacent to thiocarbonylthio group.

[B] TCEP – tris(2-carboxyethyl) phosphine hydrochloride, EDTA – ethylenediaminetetraacetic acid, TCEP – tris(2-carboxyethyl phosphine), DMPP – dimethylphenylphosphine.



Scheme 10.

should be preferred and symmetrical trithiocarbonates avoided when preparing polymers with terminal thiol functionality by RAFT polymerization followed by nucleophilic cleavage of the thiocarbonylthio group. This would minimize the production of non-functional and coupled polymers.

Aminolysis of PMMA-dithiobenzoate, as well as being complicated by coupling to provide the disulfide, is further complicated by the thiol undertaking a backbiting reaction to give a thiolactone chain end (Scheme 10).[183,480] Aminolysis in the presence of *S*-methyl methanethiosulfonate is reported to quantitatively produce PMMA with methanedithio chain ends even in non-degassed media (Scheme 10).[480] Functional methanethiosulfonates can be used in similar fashion to make the corresponding end-functional polymers. Thus, *S*-but-3-ynyl methanethiosulfonate was used to prepare an alkyne end functional polymer for use in 'click' chemistry.[89]

In other examples of this strategy, aminolysis of PNIPAM-trithiocarbonate was performed in the presence of 2,2′-dithiodipyridine to form a polymer with a pyridyl disulfide end-group in very high yield,[479] similarly, PNVP-xanthate was protected with Ellman's reagent (see section on Block Copolymers).[396] These polymers can be used to regenerate a polymer with a thiol end-group under mild conditions and/or can be used to make biopolymer conjugates by a disulfide exchange process.

The issue of removal of byproducts following end-group removal can be resolved through use of a functional reagent (e.g., a functional amine)[482] and or a Z-functional RAFT agent[483] to simplify polymer purification.

Click Reactions

Use of 'click chemistry' in polymer chemistry has recently attracted much attention.[461–464] The RAFT process can be used to synthesize polymers with clickable moieties at the chain ends through the use of RAFT agents with appropriate functionality on 'Z' or 'R'. A significant number of these papers concern the combination of RAFT and azide–alkyne 1,3-dipolar cycloaddition. Many RAFT agents with azido-functionality (**27**, **137**, **148**, **181**, **218**, **220**) or acetylene-functionality (**26**, **46**, **134**) have appeared. Ladmiral et al.[335] have posted a warning that azides also undergo 1,3-dipolar cycloaddition with common monomers (MMA, MA, NIPAM, and St were studied) and that this can occur under polymerization conditions. The use of lower reaction temperatures in polymerization can minimize this issue.

Other click reactions are:

- The thiol-ene reaction. Thiol-functional polymers are made as described above under Aminolysis/Hydrolysis/Ionic Reduction. Ene-functional RAFT agents are also possible. However, the potential for reaction during RAFT polymerization needs to be considered. Maleimide functionality may be introduced as described under Addition–Fragmentation Coupling above.
- The active ester-amine reaction. RAFT agents with active ester functionality on 'R' include: **28**, **31**, **133**.[173]
- The pyridyl disulfide-thiol reaction. RAFT agents with pyridyl disulfide functionality on 'Z' include: **181**–**184**.

RAFT agents and macro-RAFT agents with electron withdrawing 'Z' (**62**, **265**) have been shown to undergo hetero-Diels–Alder reactions with suitable dienes (Scheme 11).[209,223,224,418,419,484,485] The process has also been developed as a route to block copolymers[223,418] and star polymers.[224,418,484]

Other End-Group Modification Processes

PNVP chain ends formed with xanthate RAFT agents are susceptible to hydrolysis and can be converted into aldehyde chain ends (Scheme 12).[379] The aldehyde chain ends can be used for bioconjugation. End group stability may also be an issue during RAFT polymerization of NVP particularly at higher reaction temperatures (>60°C).

Macro-RAFT agents can be selectively end-functionalized by addition of a single monomer unit to form a new macro-RAFT agent. The strategy involves selection of monomer or reaction conditions such that there is no polymerization. Recent examples involve attachment of MAH to a PSt macro-RAFT agent[186] and a single maleimide unit to a PDMEAMA macro-RAFT agent.[426]

Statistical/Gradient Copolymers

It should be noted that, due to the effects of compositional drift, most copolymers prepared by RAFT polymerization generally fall under the description of gradient copolymers. Many examples of copolymer synthesis are included in the Tables above.

Kinetic simulations of monomer sequence distributions formed in RAFT polymerization have been performed.[266,486] Shot polymerizations were simulated to show the potential of using the RAFT process to produce copolymers with customized sequence distributions.[486] Stereogradient polymers (polymers in which the tacticity varies along the chain length) have been prepared by RAFT polymerization of TPMMA.[92]

RAFT copolymerizations of alk-1-enes with MAH have been shown to provide alternating copolymers with controlled molecular weights and relatively narrow molecular weight distributions.[314]

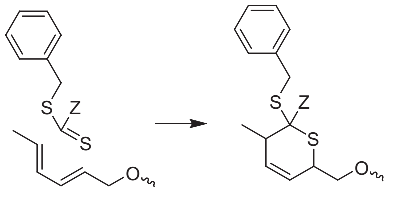
Block Copolymers

Examples of block copolymer synthesis by sequential; monomer addition are included in Tables 3–15. See also the section on Choice of RAFT agents for discussion on the importance of choosing which monomer to polymerize first when using this approach.

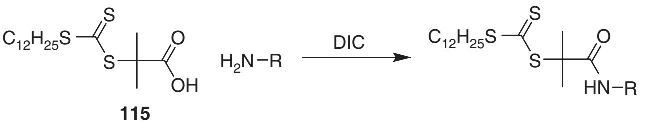
Block copolymers based on polymers formed by other polymerization mechanisms can be made by first preparing an end functional pre-polymer that is converted into a macro-RAFT agent by end-group transformation. This macro-RAFT agent is then used in the preparation of the desired block copolymer. Many examples of this strategy have now been reported. Macro-RAFT agents identified in Tables 3–15 include PEO macro-RAFT agents (**33**, **34**, **78**, **83**, **126**, **178**, **183**, **226**, **227**, **229**, **230**), PLA macro-RAFT agents (**179**, **180**), a PE macro-RAFT agent (**38**), a PIB macro-RAFT agent (**127**), poly(3-hexylthiophene) macro-RAFT agents (**99**, **186**), a poly(dimethylsiloxane) macro-RAFT agent (**187**), and a polyhedral oligomeric silsesquioxane (POSS) macro-RAFT agent (**176**).

Recently, there has also been substantial interest in the synthesis of block and graft copolymers (conjugates) with biological polymers. One approach has been to attach a RAFT agent functionality to the biopolymer so as to form a biopolymer macro-RAFT agent. Thus, BSA was converted into a macro-RAFT agent through reaction of the BSA thiol group with a pyridyl disulfide functional RAFT agent **183**[366] or the maleimide functional RAFT agent **136**.[329] These macro-RAFT agents were then used to synthesize conjugates through polymerization of NIPAM in aqueous media without denaturing the BSA.

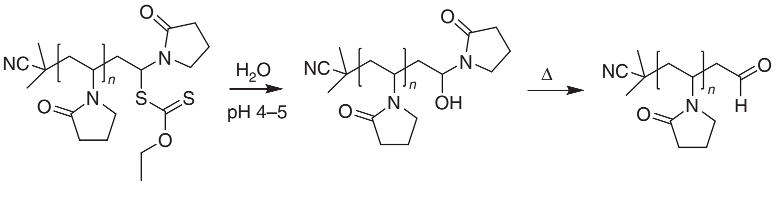
A frequently used approach to the synthesis of macro-RAFT agents is the carbodiimide-assisted coupling of carboxy-functional RAFT agents with amino- or hydroxy-functionality in the (macro)molecule of interest (e.g., Schemes 13 and 14). The same approach may be used in forming graft copolymers to polyfunctional substrates such as chitosan.[487] For additional examples see Table 30 and our previous reviews.[7,8]



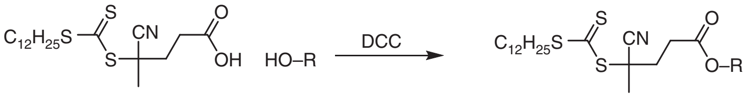
Scheme 11.



Scheme 13. (DIC = diisopropyl carbodiimide.)



Scheme 12.



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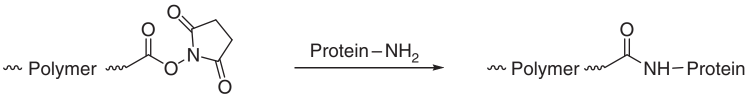
Scheme 14. (DCC = dicyclohexyl carbodiimide.)

Table 30. Conjugates by coupling reactions with acid functional RAFT agents

Initial RAFT agent	Block A[A]	Block B[B]	Ref.
Block			
115	Peptide	BA NIPAM OEGA	[488]
25	Peptide	BA	[489]
25	Polyisobutylene (**127**)	MMA St	[296]
95	Poly(3-hexylthiophene) (**99**)	**303**	[264]
Graft			
115	Chitosan	AA	[487]
115	Silica (amine modified)	MA	[490]
25	Silicon wafer (amine modified)	MMA	[179]
103*	Silicon wafer (amine modified)	NIPAM	[273]

[A] Substrate used in forming macro-RAFT agent.

[B] Monomer polymerized in presence of Block A macro-RAFT agent.



Scheme 15.

Block copolymers are also synthesized by coupling the RAFT-synthesized polymer with another polymer through functionality on either the 'R' or 'Z' groups. This is the most commonly exploited approach to make protein and other biopolymer conjugates.[491–494] Note that use of functionality on 'Z' leaves the thiocarbonylthio group as a potentially degradable link at the block juncture. This may or may not be advantageous depending on the application.

In making biopolymer conjugates, the biopolymer can be attached to a synthetic polymer having appropriate reactive functionality introduced through the use of a functional RAFT agent or attached post-RAFT polymerization by end-group transformation. Methods used include:

(a) the use of active ester end-groups to react with amino-functional proteins. RAFT agents with active ester functionality on 'R' include **28**, **30**, **31**, and **133** (Scheme 15).
(b) pyridyl disulfide end-groups with thiol functional proteins. RAFT agents with pyridyl disulfide functionality on 'Z' include **105**[282] and **181**–**184** (Scheme 16).
(c) thiol-ene chemistry with thiol functional proteins. Maleimide functionality may be introduced post polymerization with use of addition–fragmentation coupling to replace a trithiocarbonate end-group (Scheme 17).[368,374]
(d) azide–alkyne click chemistry. The stragegy requires attachment of alkyne (or azide) functionality to the protein. Azide-functional RAFT agents used in this context include **137**[331,332] and **181** (Scheme 18).[364]
(e) the attachment of ligands that show specific protein binding, for example, that of biotin with streptavidin (Scheme 19). RAFT agents incorporating biotin include **56**[211,212] and **185**.[368] The biotin moiety has also been attached post polymerization by azide–alkyne click chemistry[364] or by thiol-ene chemistry.[412]
(f) conversion of thiocarbonylthio groups of RAFT-synthesized polymers into thiol functionalities which are then used for conjugation. The thiol-end-groups were protected by reaction with Ellman's reagent [5,5′-dithiobis-(2-nitrobenzoic acid)] which also activates the thiol for reaction with a thio functional biopolymer (ssDNA, peptide) by disulfide exchange (Scheme 20).[396]

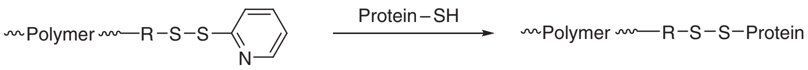
Most of these same approaches have also been used in making other (non-biopolymer) block, star, and graft copolymers.

The synthesis of block copolymers by a combination of ATRP and RAFT has been reported. Several groups[495,496] have reported processes where a first block comprising a 'more activated monomer' is prepared by ATRP and then a second block comprising a 'less activated monomer' is prepared by RAFT (e.g., PtBA-*b*-PVAc, Scheme 21[495] or PSt-*b*-PNVP[496]). Sequential ATRP and RAFT has also been used to prepare block copolymer brushes.[497]

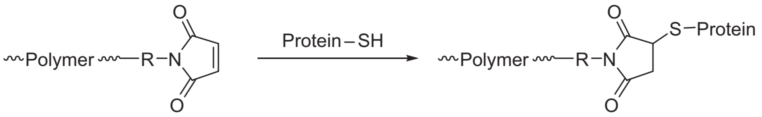
Matyjaszewski and coworkers[498] used a compound that combined a RAFT agent and an ATRP initiator functionality in the one molecule to synthesize PVAc-*b*-PMA (Scheme 22). Tong et al.[499] used a similar approach in the synthesis of PSt-*b*-PVAc. Other permutations of this approach were also explored.[498] The methodology was unsuccessful for PMMA-*b*-PVAc which was attributed to inefficient initiation of VAc polymerization by the PMMA propagating radical.

Multiblock Copolymers

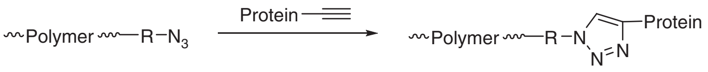
There have been several new reports on the synthesis of multiblock copolymers by RAFT polymerization using poly-RAFT



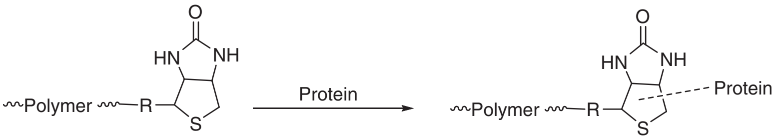
Scheme 16.



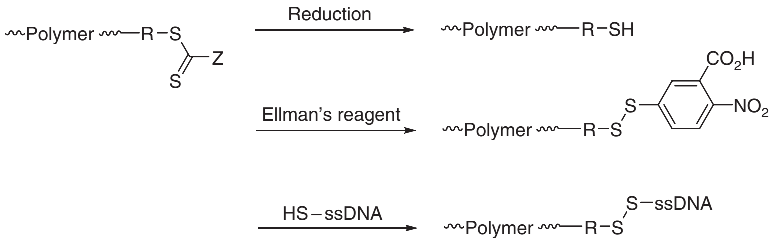
Scheme 17.



Scheme 18.



Scheme 19.



Scheme 20.

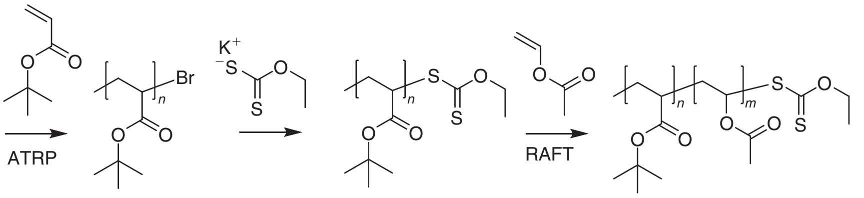
Table 31. Biopolymer conjugates by coupling reactions

RAFT agent (Block A)[A,B,C]	Block B	Coupling reaction	Ref.
137 (NIPAM, DMAM)	Propargyl folate	Azide-alkyne click	[332]
137 (NIPAM)	BSA	Azide-alkyne click	[331]
54 (NAM)	Protein	Biotin conjugation	[211]
182 (PEGA)	siRNA	Pyridyl disulfide	[365]
181 (NIPAM)	BSA, avidin (heterotelechelic)	1. Pyridyl disulfide, 2. azide-alkyne click	[364]
166 (AA-*b*-NIPAM)	Streptavidin	Biotin conjugation	[412]
189 (NIPAM/**321**)	BSA (telechelic)	Thiol-ene	[374]
185 (NIPAM)	Streptavidin, BSA (heterotelechelic)	1. Thiol-ene, 2. biotin conjugation	[368]
228 (NVP)	ssDNA	RAFT end reduction/thiol coupling	[396]

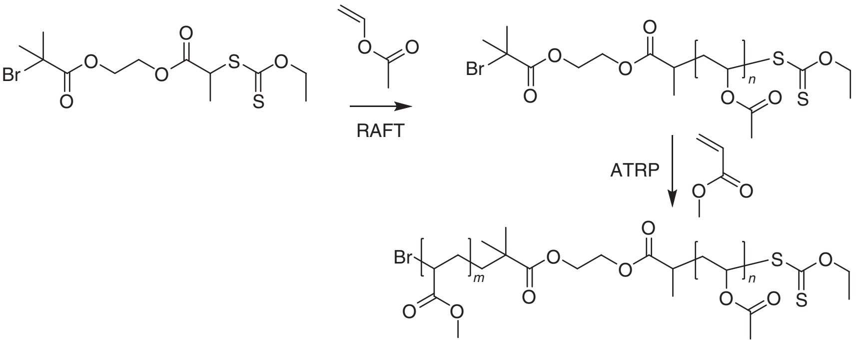
[A] See footnote A of Table 3.
[B] See footnote B of Table 3.
[C] Monomers shown in parentheses were subjected to RAFT polymerization in the presence of the indicated RAFT agent.

agents (polymers with in chain thiocarbonylthio functionality). One example is the poly(dimethylsiloxane) multiblock made using **396** as shown in Scheme 23.[500] Other examples are mentioned in Table 32.

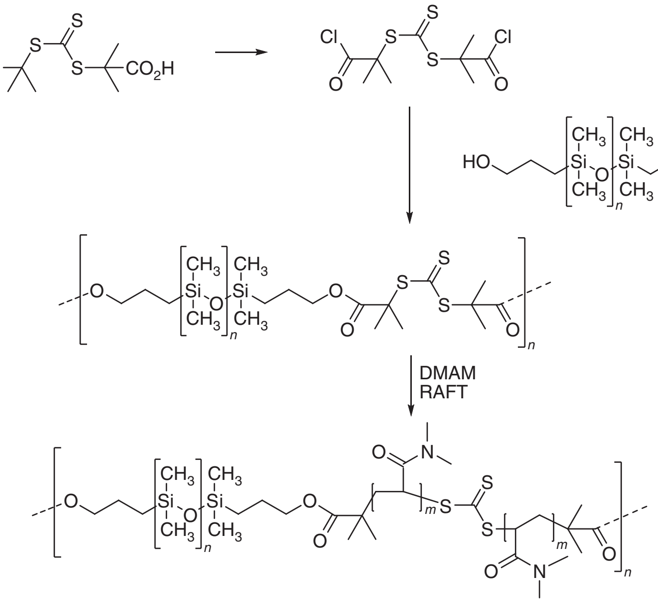
Further examples of cyclic trithiocarbonates have been reported as precursors to poly-RAFT agents (Table 33). Trithiocarbonate **400** was used to prepare multiblock copolymers of P4VP and PSt by sequential monomer addition.[501,502] RAFT polymerization with the cyclic trithiocarbonates (**400**–**402**) provides polymers of high dispersity (e.g., $Đ_M \sim 6$ for PSt prepared with **402**) with multiple trithiocarbonate units per chain, although individual segments have relatively low dispersity ($Đ_M < 1.3$). Low temperature polymerization of MA or St in the presence of the cyclic xanthate (**403**) produced mixtures of cyclic and linear polymer that contain only one residue from **403** per chain.[503]



Scheme 21. ATRP/RAFT combination for block copolymer synthesis.



Scheme 22. ATRP/RAFT combination for block copolymer synthesis.



396

Scheme 23.

Another RAFT-based approach to multiblock copolymers is based on oxidative coupling of telechelic polymers with thiol end-groups.[196,240–242,260] The telechelics are synthesized by RAFT polymerization making use of a bis-RAFT agent with subsequent end-group transformation to form the bis-thiol. The procedure was also applied to synthesize cyclic polymers by using high dilution conditions.[260]

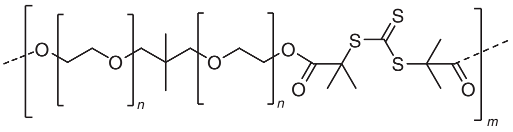
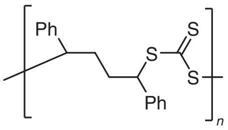
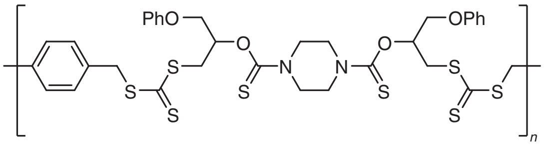
Star Polymers

The literature on the synthesis of star polymers using the RAFT process continues to grow rapidly. In this section we consider syntheses that begin with a substrate containing multiple thiocarbonylthio groups of appropriate design, a multi-RAFT agent, and 'grafting-to' syntheses that involve coupling of RAFT-made polymers to a core or arms of defined structure. Formation of star nano- or microgels by copolymerization with a divinyl monomer, by self-assembly and crosslinking of block copolymers or by growth from a crosslinked polymer or a nanoparticle core is covered in the next section, Microgels and Nanoparticles.

Use of Multi-RAFT Agents

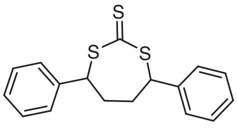
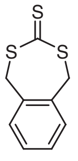
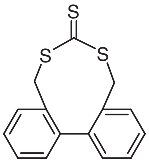
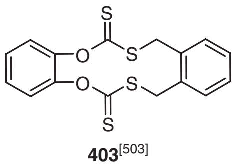
The multi-RAFT agent may in principle be a small organic compound, an organometallic complex, a dendrimer, a hyperbranched species, a macromolecular species, a particle or indeed any moiety that possesses multiple thiocarbonylthio groups. Of these, macromolecular species and particles are considered in

Table 32. Poly-RAFT agents

Poly-RAFT agent	Polymerizations[A,B]
396[500]	DMAM[500]
 **397**[504,505]	St[504,505] St-*b*-tBA[505]
 **398**[475]	St[475] DMA[475] DMA-*b*-NIPAM[475]
 **399**[475]	St[376]

[A] See footnote A of Table 3.
[B] See footnote B of Table 3.

Table 33. RAFT agents and RAFT polymerizations – cyclic RAFT agents

RAFT agent	Polymerizations[A,B]	RAFT agent	Polymerizations[A,B]
 **400**[501]	BA[506] St[501] 4VP[501] St-*b*-4VP[501,502] 4VP-*b*-St[501]	 **401***	BA[506] MA[507]
 **402**[508]	St[508]	 **403**[503]	MA[503] St[503]

[A] See footnote A of Table 3.
[B] See footnote B of Table 3.

the section on Polymer Brushes below. Recent examples of star cores are shown in Table 4 and Table 6 (dithioesters), Table 9 (trithiocarbonates), and Table 11 (xanthates).

The first publications in this field[6] recognized two limiting forms of star (or graft/brush copolymer) growth depending on the orientation of the thiocarbonylthio group with respect to the core.

In the first strategy, the propagating radicals are linear chains that dissociate from the core. ‘Z’-connected RAFT agents (**404**, Scheme 24) are employed. The advantage of this strategy is that by-products from star–star coupling are unlikely. The thiocarbonylthio functionality is retained at the core of the star. A potential disadvantage of the ‘propagation away from core’ strategy is that reactions that cleave the thiocarbonylthio groups (e.g., aminolysis and thermolysis) cause destruction of the star structure (i.e., loss of the arms, Scheme 24). This feature can also be used to advantage in developing supported polymer syntheses or degradable network polymers (see Polymer Networks). A further potential issue is that the thiocarbonylthio functionality may become sterically inaccessible as the polymerization proceeds.

In the second strategy most propagating radicals remain attached to the core and ‘R’-connected RAFT agents (**405**, Scheme 25) are used. Most thiocarbonylthio functionality remains on the periphery of the star. However, a linear macro-RAFT agent is released to the polymerization medium by the RAFT process. Since propagating radicals are attached to the core, termination by star–star coupling is a complication. Because the thiocarbonylthio groups are end-groups, they can be cleaved (e.g., by aminolysis) without destroying the star structure (Scheme 25).

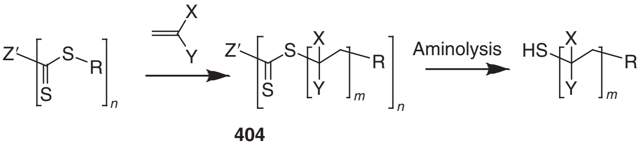
The advantages and disadvantages of the two approaches are considered in detail in several recent papers.[20,248,256,259,268,377,509–511] It is clear that the relative importance of the various factors mentioned above depends strongly on the particular monomer and RAFT agent used.

The leaving group ability of 'R' has been shown to have a significant effect on the molecular weight distribution of the arms. For 'Z'-connected PSt stars formed with multi-RAFT agents (type **405**) with R′ = benzyl (a relatively poor radical leaving group) the dispersities for the cleaved arms distribution is relatively broad even though the dispersity of the star polymers is narrow.[377] Substantially lower dispersities for the cleaved arms are seen for the similar RAFT agent with R′ = phenylethyl.[377] It is known that RAFT agents with R = phenylethyl have transfer constants an order of magnitude higher than those with R = benzyl.[56]

Stars in which the arms are connected to the core through ionic bonding have been described.[512,513] The approach has been exploited in synthesizing mikto-arm star polymers.[513] Thus, the PSt macro-RAFT agent **406** (Fig. 6) was used to make a mikto-arm star with PSt and PNIPAM arms. The ionic bonded arms were stable during RAFT polymerization and in solution surviving characterization by gel permeation chromatography. However, the PNIPAM arms were readily released from the core by treating the polymer with acid.[502]

Star Polymers by 'Grafting-To'

Various combinations of RAFT, ATRP, click, ring opening polymerization, and other methods have been used to synthesize star polymers, including mikto-arm stars.[174,223,224,330,418,514] Hetero-Diels–Alder coupling was used to synthesize a 12-armed star as shown in Scheme 26 from a star polymer precursor prepared by ATRP and a PSt macro-RAFT agent.[418]



404

Scheme 24. Star polymer synthesis by the 'propagation away from core' strategy using a 'Z'-connected RAFT agent.

Microgels and Nanoparticles

In this section we consider direct formation of polymer microgels or nanoparticles in a solution polymerization process or by self-assembly and crosslinking of block copolymers. Surface functionalization of nanoparticles by RAFT polymerization is considered in the next section. Formation of particles and nanoparticles by heterogeneous polymerization (emulsion and miniemulsion polymerization) is discussed above.

The synthesis of nanoparticles by block copolymer self assembly and crosslinking of micelles so formed has been reported by several groups. Examples are included in Table 34.

Polymeric nanoparticles were prepared through the chain collapse of linear polymers driven by noncovalent crosslinking of copolymers that contain dendritic self-complementary hydrogen-bonding monomers (**283** and **284**).[197] The behaviour observed was strongly dependent on the level of incorporation of the dendritic monomers.

One of the more popular methods for forming core-crosslinked star polymers (microgels, nanogels) involves (co)polymerization of a divinyl monomer using some form of reversible deactivation polymerization.[516,517] Examples of this strategy in combination with RAFT polymerization include the synthesis of drug delivery vehicles involving use of an acid cleavable crosslinker **407**[105] or the biodegradable crosslinker **408**[142] (Fig. 7) and the synthesis of PSt star polymers with active ester groups on the periphery by making use of RAFT agent **133**.[325] Other recent examples of applying this strategy are included in Table 35.

The formation of so-called capsosomes (liposome-compartmentalized polymer capsules) has been described. The process involved liposomes being sandwiched between a cholesterol-modified poly(L-lysine) precursor layer and a RAFT-synthesized poly(methacrylic acid)-*co*-(cholesteryl methacrylate) capping layer.[295]

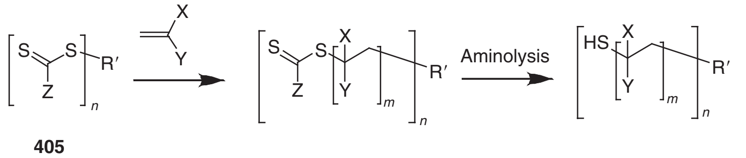
RAFT polymerization may be used to grow arms on crosslinked cores formed by RAFT or other processes. For example, hyperbranched poly(glycerol) core functionalized with an azo-initiator and an ATRP initiator functionality was used to sequentially form arms by RAFT polymerization and ATRP to provide a mikto-arm structure.[519]

Polymer Brushes/Graft Copolymers/Comb Polymers/Surface Modification

Grafting-From Processes

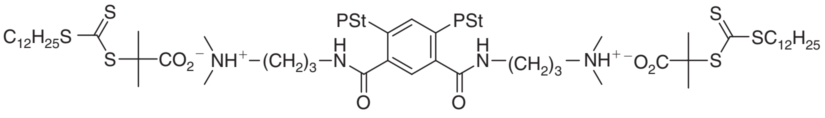
The grafting-from approach involves attachment of a RAFT agent functionality to a surface and using this material as a macro-RAFT agent in polymerization. A variant on this approach is to attach initiator functionality which is then used to generate a macro-RAFT agent in situ during a RAFT polymerization.

The synthesis of polymer–silica nanocomposites has been reviewed.[520] A variety of methods have been used to synthesize



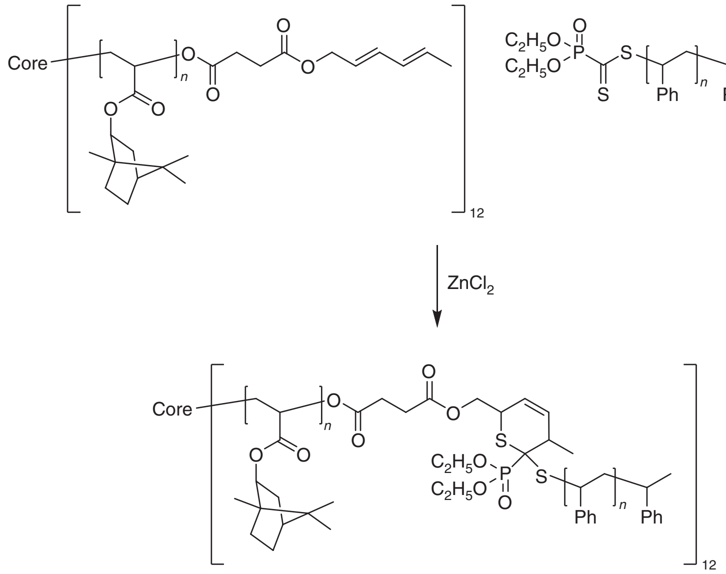
405

Scheme 25. Star polymer synthesis by the 'propagation attached to core' strategy using a 'R'-connected RAFT agent.



406 (PSt = polystyrene)

Fig. 6.



Scheme 26.

Table 34. Examples of synthesis of microgels by block copolymer self-assembly and crosslinking

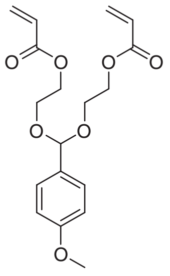
Block copolymer[A,B]	Crosslinking process	Ref.
AA-*b*-St	Diamine/carbodiimide crosslinking of PAA shell	[200]
AA-*b*-St **373**	Diamine/carbodiimide of PAA shell	[201]
tBA-*b*-**338**[235]	Diamine/carbodiimide crosslinking of PAA shell	[235]
DMAM-*b*-**331**-*b*-NIPAM	Ionic crosslinking of P**331** shell with cationic PVBTAC	[159]
DMAM-*b*-(NIPAM/**339**)	Ionic crosslinking of P(NIPAM/P**339**) shell with cationic PVBTAC	[319]
DMAEMA-*b*-NIPAM	Au crosslinking of PDMAEMA shell	[143]
MA-*b*-NAS/NAM	Diamine crosslinking of active ester in NAS/NAM shell	[299]
St/MAH-*b*-Ip	Radical crosslinking (AIBN) of PIp shell	[315]
PEG-*b*-(CEA/DEMEMA)	Photo-crosslinking of P(CEA/DEMEMA) core	[515]

[A] See footnote A of Table 3.

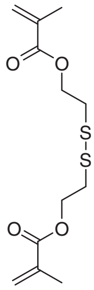
[B] See footnote B of Table 3.

silica-bound RAFT agent functionality for surface-initiated grafting (Table 36). Several papers have appeared on the synthesis of brushes on silica nanoparticles using combinations of click chemistry and RAFT.[326,327,521] Ranjan et al.[326,521] reported on three variants. In the first 'grafting-to' approach, polymers made with RAFT agent were coupled to azide-functional silica particles. In the second 'grafting-from' approach polymers were grown from the silica particle bound RAFT agent (Scheme 27). In the third 'tandem' approach a click reaction and a RAFT polymerization step were performed simultaneously.

Mesoporous silica beads modified with an azo initiator (Scheme 28) were used to initiate RAFT polymerization of NIPAM mediated by benzyl dithiobenzoate.[219] The beads were evaluated as a thermoresponsive chromatographic support.



407[105]



408[142]

Fig. 7.

Other substrates to which the 'grafting-from' approach has been applied include silicon wafers,[179,213,524] poly(silsesquioxane),[210,228] polyhedral oligomeric silsesquioxane (POSS),[350,360,361] indium-tin oxide (ITO) surfaces,[176] carbon nanotubes,[525] titania particles,[526,527] clay,[528–530] cadmium sulfide nanoparticles,[531] cellulose,[532–535] and PVDF membranes.[536]

Table 35. Recent examples of synthesis of core-crosslinked star polymers by RAFT-mediated radical crosslinking polymerization

Arm monomer[A,B]	RAFT agent[C]	Crosslinker	Ref.
AEMA	**25**	**408** Divinylsulfone	[142]
319	**168**	Hexanediol diacrylate	[352]
AA	**211**	Methylene-bis-acrylamide	[397]
BA	**22**	**407**	[105]
St	**39**	Divinylbenzene/4VP	[184]
St	**109**	Divinylbenzene	[284]
St	**133**	Divinylbenzene	[325]
St St-*b*-NIPAM	**61**	Divinylbenzene	[518]
PEO	**38**	Divinylbenzene/S	[180]
PEO-*b*-DMAM PEO-*b*-DEAM PEO-*b*-DMAM-*b*-DEAM	**138**	Methylene-bis-acrylamide/DEAM	[333]
VAc	**211**	Divinyl adipate	[388]

[A] See footnote A of Table 3.

[B] See footnote B of Table 3.

[C] RAFT agent used in synthesis of arm macro-RAFT agent.

A RAFT agent with a pendent norbornene was polymerized by ROMP and the product used in RAFT polymerization to form a comb with P(St/MAH)-*b*-PSt arms.[323] Monomers with ATRP initiator functionality (**323**) have been subjected to RAFT polymerization and the polymers formed used in ATRP to form comb polymers.

RAFT agent functionalized silicon wafers were prepared by treatment of the wafer with RAFT agents having methoxysilane (**59**, **84**, or **97**),[213] or active ester (**31**)[179] functional groups on 'R' or with TMSPMA, AIBN, and phenylethyl dithiobenzoate (**49**) in a one-step process.[537] Silicon wafers have also been modified with potassium *O*-ethylxanthate and this was used to form surface-initiated MMA grafts.[524] The result is surprising because xanthates are generally not useful for controlling MMA polymerization.

Radiation-induced graft polymerization is believed to involve formation of initiating species on the substrate, which then initiate polymerization. Thus, further examples of a grafting-from approach are gamma-initiated grafting of styrene[438] or SSO3Na[167] from cellulose, and tBA from commercial ethylene propylene copolymer[439] in the presence of RAFT agent **92**.

Grafting-To Processes

One use of RAFT polymerization in the 'grafting-to' approach involves the synthesis of polymers with reactive end-groups or block structures by RAFT polymerization, which are then self-assembled and/or bonded to a particle, surface, or other structure. This approach has been used to make inorganic (TiO_2, SnO_2 or ZnO) nanorods[102] or CdSe/ZnS quantum dots[538] with PAA-*b*-PSt,[539] P(AEME-*co*-**328**-*co*-**342**)[278] or semiconductor (P**364** or P**365**) arms, gold nanoparticles with PSt,[476] PSt-*b*-P2VP,[198] PDMAEMA, PAA, or PSt,[91] P(**340**-*co*-AM) or P(**341**-*co*-AM),[239] PPEGA-*b*-PNIPAM,[217] PMMA-*b*-PNIPAM,[189] or P(DEGMA-*co*-tBA), P(DEGMA-*co*-tBA)-*b*-PGMA, PGMA, PSt[398] grafts, magnetic iron with PNIPAM grafts,[305] silver nanoparticles with PSt grafts,[409] chitosan with PAA grafts,[487] and silicon wafers with NIPAM grafts.[273] Silicon wafers and silica particles have also been modified with multiple layers of an amine-functional polymer, polyethyleneimine or poly(allylamine hydrochloride), respectively, and PAA-*b*-PSSO3Na in a layer-by-layer assembly process.[354]

A second way that RAFT is applied in a 'grafting-to' approach involves the use of RAFT copolymerization to synthesize a functional scaffold to which other polymers and or functionality are subsequently attached.

RAFT polymerization has been used to synthesize the scaffolds for attachment of biopolymers by copolymerization of monomers shown in Table 24 (azide or alkyne functionality), Table 25 (active ester functionality, e.g., Scheme 29) for attachment of therapeutic agents,[317] peptides,[160,317] or DNA,[347] or Table 26 (e.g., pyridyl disulfide functionality (**391**), Scheme 30) for attachment of thiol residues of proteins (e.g., BSA),[162] or drug molecules.[161] The production of such scaffolds by RAFT and other RDRP processes for post polymerization modification has recently been reviewed.[540]

The general approach has wide application and has, for example, been used in the synthesis of photochromic polymers by coupling of spiropyran moieties to RAFT-synthesized P(BMA-*co*-HEMA).[106]

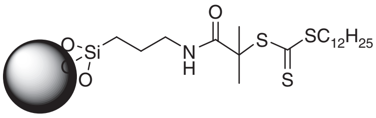
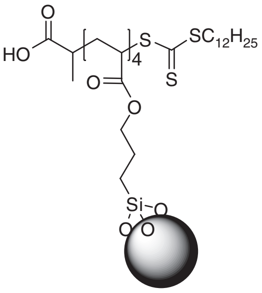
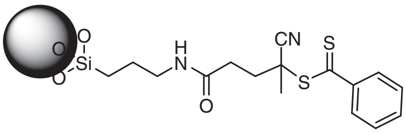
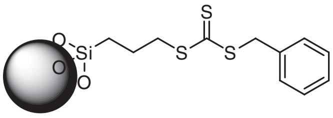
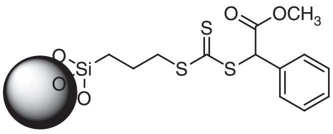
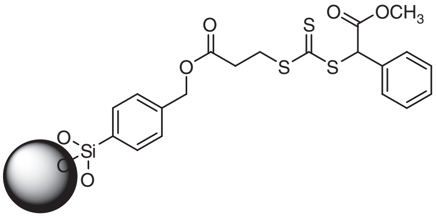
Grafting-Through Processes

This approach requires attaching monomer functionality to the substrate which may be:

- A polymer chain (Table 37). Macromonomers used in RAFT polymerization include the valine-proline-glycine-valine-glycine (VPGVG) pentapeptide macromonomer **416**,[163,164] the oligo(2-ethyl-2-oxazoline) macromonomer **417**,[112] and the polycaprolactone (PCL) macromonomer **419**.[363] The pH-sensitive dexamethasone-containing peptide macromonomer **420** has been synthesized and copolymerized with HPMA.[274] The conjugate was said to be an effective anti-arthritis therapy.
- Particles and surfaces. Nanocomposite materials have been prepared by the grafting-through polymerization of acrylate-[527] or methacrylate-functional[541] titania particles or methacrylate-functional silica particles.[542]

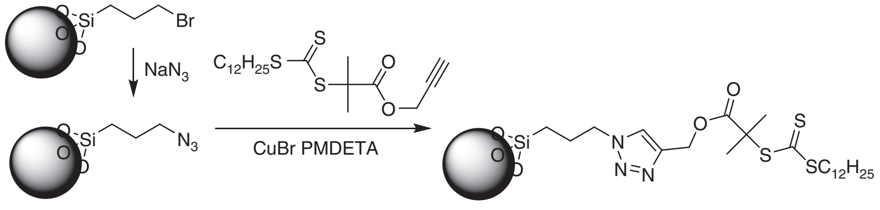
The process of formation of polymers that contain active ester functionality or pyridyl disufide functionality as substrates for grafting-to processes (see above) can be considered as additional examples of grafting-through processes.

Table 36. Silica bound RAFT agents

RAFT agent[A]	Polymerizations[B]
‘R’-attached	
409[327]	St[327] St-*b*-MA[327]
 **410**[490]	MA[490]
 **411**[340]	St[340]
 **412**[136]	**375**[136] **375**-*b*-MMA[136]
‘Z’-attached	
 **413**[522]	MA BA (MMA) St DMA NIPAM[522]
 **414**[522]	MA BA MMA St DMA NIPAM[522]
 **415**[523]	MA BA MMA St BA-*b*-MA MA-*b*-BA MMA-*b*-MA MMA-*b*-St St-*b*-MA[523]

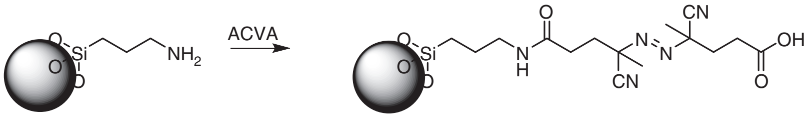
[A] See footnote A of Table 3.

[B] See footnote B of Table 3.

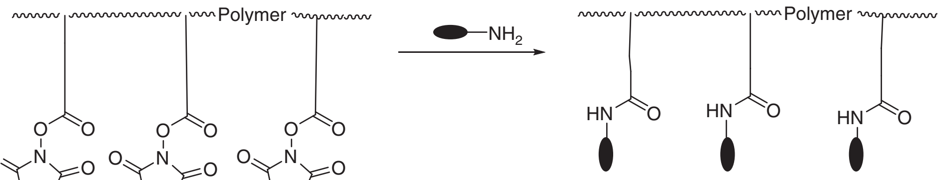


409

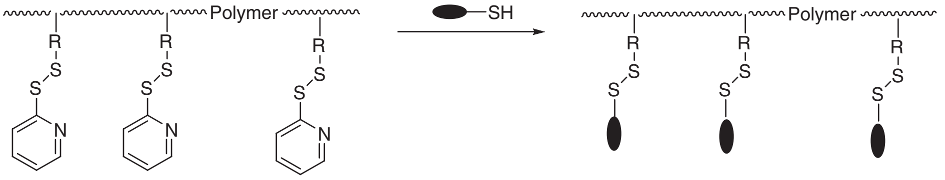
Scheme 27.



Scheme 28.



Scheme 29.



Scheme 30.

Polymer Networks

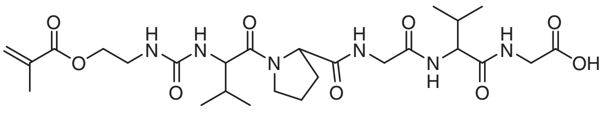
Polymer networks can be formed by crosslinking RAFT-synthesized homopolymers, block copolymers,[95,243,370] or star polymers[267] or can be formed directly by a RAFT (co)polymerization in te presence of crosslinking monomer (e.g., a divinyl monomer, ethylene glycol dimethacrylate, methylene-bis-acrylamide).[544,545] A wide variety of crosslinking processes have been explored. Polymer networks have applications in the controlled release of, for example, pharmaceuticals. Physically crosslinked hydrogel networks can be prepared by the assembly of RAFT-synthesized triblock copolymers.[86,272,546–548] The structures can be tuned to absorb either hydrophilic or hydrophobic substrates and to swell in specific media or in response to various stimuli such as pH, temperature, ionic strength, etc. by appropriate monomer selection.

Networks based on stars[267] or triblock copolymers[546] with trithiocarbonate linking groups can be degraded by aminolysis to form a polymer with thiol end-groups which is a precursor to a redox-responsive network that can be formed (through disulfide crosslinking) and degraded by addition of an oxidizing- or a reducing-agent, respectively.[267,546]

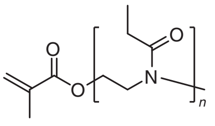
Other applications are in the area of

- photo-embossing.[549] Photo-embossed surface relief structures with significantly improved aspect ratios were prepared by addition of a RAFT agent (**23**) to a polymerization mixture of benzyl methacrylate and dipentaerythritol penta/hexa-acrylate. The RAFT photo-embossing process also proved less sensitive to air.
- production of molecularly imprinted monolithic chromatographic columns.[550] The monoliths were formed by copolymerization of MMA and ethylene glycol dimethacrylate in the presence of RAFT agent **110** and a template molecule. The use of RAFT polymerization allows better control over pore size distribution and provided columns with better resolution.
- polymer network liquid crystals.[551] Devices were formed by polymerization of hexanediol diacrylate in the presence of PSt macro-RAFT agents of various molecular weights and the nematic liquid crystal on an ITO glass substrate.

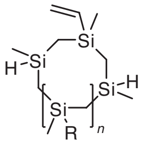
Table 37. Macromonomers subjected to RAFT polymerization



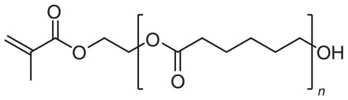
416 Peptide macromonomer[163,164]



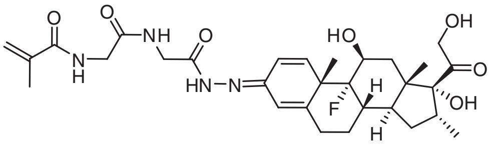
417[112]



418 Vinylcyclosilazane, R = H or $\mathrm{CH_3}$, *n* ~20[543]



419 PCL macromonomer[363]



420[274]

Conclusions

In the past two and a half years we have seen a substantial expansion in the number of papers on applications of RAFT polymerization. These applications cover areas ranging from biomedical to electronics and photonics to coatings and rheology control agents. At the same time, we have not seen any reduction in the number of papers that explore RAFT polymerization as a technique but rather we have seen an increase as people seek both to improve the process and further define the intimate details of the RAFT mechanism.

Abbreviations

Abbreviations: AcS: 4-acetoxystyrene, AA: acrylic acid, AAEMA: 2-(acetoacetoxy)ethyl methacrylate, AEMA: 2-aminoethyl methacrylate hydrochloride (**273**), AEMAM: *N*-(2-aminoethyl)methacrylamide hydrochloride (**275**), AEP: 2-(acryloyloxy)ethyl phosphate, AIBN: azoisobutyronitrile, ACHN: azobis(1-cyclohexanenitrile), ACVA: azobis(cyanovaleric acid), AM: acrylamide, AMA: allyl methacrylate, AMPS: 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS), AN: acrylonitrile, APMAM: *N*-(3-aminopropyl)methacrylamide hydrochloride (**274**), ATRP: atom transfer radical polymerization, BA: butyl acrylate, BAM: *N*-butylacrylamide, BP: β-pinene, CA: cholesteryl methacrylate (**322**), CIDNP: chemically induced nuclear polarization, CMS: 4-(chloromethyl) styrene, CMA: cholesteryl methacrylate (**309**), CPA: 3-chloropropyl acrylate, DA: dodecyl acrylate, DADMAC: diallyldimethylammonium chloride, Dc: dec-1-ene, DEAM: *N*,*N*-diethylacrylamide, DEGMA: (diethylene glycol monomethyl ether) methacrylate, DEHEA: di(ethylene glycol) 2-ethylhexyl ether acrylate, $Đ_\mathrm{M}$: molar-mass dispersity = ratio of weight average to number average molecular weight,[552] DMAM: *N*,*N*-dimethylacrylamide, DMAEA: 2-(dimethylamino)ethyl acrylate, DMAEMA: 2-(dimethylamino)ethyl methacrylate, DMAPMAM: *N*-(3-(dimethylamino)propyl)methacrylamide hydrochloride, DPAEMA: 2-(diisopropylamino)ethyl methacrylate, EA: ethyl acrylate, EAA: ethyl α-acetoxyacrylate, E: ethene, EEA: ethoxyethyl acrylate, EGMA: (ethylene glycol monomethyl ether) methacrylate, EHA: 2-ethylhexyl acrylate, EMAM: *N*-ethyl-*N*-methylacrylamide, EVC: *N*-ethyl-3-vinylcarbazole, EVE: ethyl vinyl ether, GMA: glycidyl methacrylate, HEA: 2-hydroxyethyl acrylate, HEMA: 2-hydroxyethyl methacrylate, HMA: hexylmethacrylate, HMS: 4-(hydroxymethyl)styrene, HPMAM: *N*-hydroxypropyl methacrylamide, iBA: isobornyl acrylate, iBMA: isobutyl methacrylate, Ip: isoprene, LAM: less activated monomer (includes vinyl monomers such as VAc, NVP, and NVC), LMA: dodecyl methacrylate, MA: methyl acrylate, MADIX: Macromolecular Design by Interchange of Xanthate, MAEP: 2-(methacryloyloxy)ethyl phosphate, MAH: maleic anhydride, MAM: more activated monomer (includes styrenes, acrylates, acrylamides), MMA: methyl methacrylate, MMBL: γ-methyl-α-methylene-γ-butyrolactone (**290**), MPC: methacryloyloxyethyl phosphorylcholine (**292**), MVK: methyl vinyl ketone, NAM: *N*-acryloylmorpholine, NAPM: *N*-acryloyl-L-proline methyl ester, NAPAM: *N*-acryloyl-L-phenylalanine methyl ester, NAP: *N*-acryloylpyrrolidine, NAS: *N*-acryloyloxysuccinimide, NEMI: *N*-ethylmaleimide, NIPAM: *N*-isopropylacrylamide, NIPMAM: *N*-isopropylmethacrylamide, NMMI: *N*-methylmaleimide, NMP: nitroxide mediated polymerization, NPMI: *N*-phenylmaleimide, NMS: *N*-methacryloyloxysuccinimide, NVC: *N*-vinylcarbazole, NVCL: *N*-vinylcaprolactam, NVP: *N*-vinylpyrrolidone, NVPI: *N*-vinylphthalimide, PAM: *N*-propylacrylamide, PA: propargyl acrylate (**372**), PAA: α-propylacrylic acid (2-methylenepentanoic acid), PE: polyethylene, PEG: poly(ethylene glycol) monomethyl ether, PEGA: (poly(ethylene glycol) monomethyl ether) acrylate, PEGMA: (poly(ethylene glycol) monomethyl ether) methacrylate, PEO: poly(ethylene oxide), PFMA: pentafluorophenyl methacrylate, PFS: pentafluorophenylstyrene, PIB: polyisobutylene, PLA: poly(lactic acid), PMA: propargyl methacrylate, POSS: isobutyl polyhedral oligomeric silsesquioxane, PVK: phenyl vinyl ketone, RAFT: reversible addition fragmentation chain transfer, RDRP: reversible deactivation radical polymerization, SB: 4-(3-butenyl)styrene, siRNA: short interfering ribonucleic acid, SMe: 4-methylstyrene, ssDNA: single stranded deoxyribonucleic acid, SSO3Na: sodium styrene-4-sulfonate, St: styrene; TBAM: *N*-*tert*-butylacrylamide, TFPMA: 2,2,3,3-tetrafluoropropyl methacrylate, TFPA: 2,2,3,3-tetrafluoropropyl acrylate, THPA: tetrahydropyran, TMSEMA: 2-(trimethylsilyloxy)-ethyl methacrylate, TMSPMA: 3-(trimethoxysilyl) propyl methacrylate, tBA: *tert*-butyl acrylate, tBS: 4-(*tert*-butoxy)styrene, TMAEMA: 2-(trimethylamonium)ethyl methacrylate, TMAPMA: 3-(trimethylamonium)propyl methacrylate, TPMMA: triphenylmethyl methacrylate (**302**), VAc: vinyl acetate, VB: vinyl butyrate, VBA: 4-vinylbenzoic acid, VBSC: 4-vinylbenzenesulfonyl chloride, VBDA: (4-vinylbenzyl)dimethylamine, VBTAC: (*ar*-vinylbenzyl) trimethylammonium chloride (**351**), VBTPC: (4-vinylbenzyl) trimethylphosphonium chloride (**359**), 2VP: 2-vinylypyridine, 4VP: 4-vinylpyridine. Polymer abbreviations are formed by adding the suffix 'P' to the corresponding monomer abbreviation. Thus PMMA: poly(methyl methacrylate).

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