

Feature Article

Radical addition–fragmentation chemistry in polymer synthesis

Graeme Moad*, Ezio Rizzardo*, San H. Thang*

CSIRO Molecular and Health Technologies, Bayview Avenue, Clayton, Victoria 3168, Australia

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Abstract

This review traces the development of addition–fragmentation chain transfer agents and related ring-opening monomers highlighting recent innovation in these areas. The major part of this review deals with reagents that give reversible addition–fragmentation chain transfer (RAFT). These reagents include dithioesters, trithiocarbonates, dithiocarbamates and xanthates. The RAFT process is a versatile method for conferring living characteristics on radical polymerizations providing unprecedented control over molecular weight, molecular weight distribution, composition and architecture. It is suitable for most monomers polymerizable by radical polymerization and is robust under a wide range of reaction conditions. It provides a route to functional polymers, cyclopolymers, gradient copolymers, block polymers and star polymers.

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Keywords: Addition–fragmentation chain transfer; RAFT polymerization; Ring-opening polymerization

Abbreviations: AA, acrylic acid; AcN, acenaphthalene; ACP, azobis(2-cyanopentanoic acid); AEMA, 2-aminoethyl methacrylate hydrochloride; AIBN, azobis(isobutyronitrile); AIBMe, azobis(methyl isobutyrate); AM, acrylamide; AMBA, sodium 3-acrylamido-3-methylbutanoate; AMPS, sodium 2-acrylamido-2-methylpropane-1-sulfonate; AMS, α -methylstyrene; AN, acrylonitrile; B, butadiene; BA, butyl acrylate; BMA, butyl methacrylate; BMDO, 5,6-benzo-2-methylene-1,3-dioxepan; BuAc, butyl acetate; BzMA, benzyl methacrylate; DA, dodecyl acrylate; DADMAC, diallyldimethylammonium chloride; DAGMA, 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucosofuranose (diacetone glucose methacrylate); DBI, di-*n*-butyl itaconate; DEAM, *N,N*-diethylacrylamide; DEGA, 2-(2-ethoxyethoxy)ethyl acrylate ((diethyleneglycol ethyl ether) acrylate); DEGMA, 2-(2-methoxyethoxy)ethyl acrylate; DMAM, *N,N*-dimethylacrylamide; DMAEMA, *N,N*-(dimethylamino)ethyl methacrylate; DMAPMAM, *N*-[3-(dimethylamino)propyl]methacrylamide; EA, ethyl acrylate; EAA, ethyl- α -acetoxyacrylate; EHA, 2-ethylhexyl acrylate; EHMA, 2-ethylhexyl methacrylate; EMAM, *N*-ethyl-*N*-methylacrylamide; GMA, glycidyl methacrylate; HEA, 2-hydroxyethyl acrylate; HEMA, 2-hydroxyethyl methacrylate; HPMAM, *N*-(2-hydroxypropyl) methacrylamide; Ip, isoprene; I, initiator; *i*-BMA, *iso*-butyl methacrylate; *i*-OA, *iso*-octyl acrylate; *i*-PrOH, propan-2-ol; *L*, fraction of living chains; LMA, lauryl methacrylate lauryl (dodecyl methacrylate); LA, lauryl (or dodecyl) acrylate; M, monomer; MA, methyl acrylate; MAA, methacrylic acid; MAH, maleic anhydride; MEP, 2-methacryloylethyl phosphoric acid; MAM, methacrylamide; MMA, methyl methacrylate; MMT, montmorillonite; MVK, methyl vinyl ketone; NAM, *N*-acryloylmorpholine; NAP, *N*-acryloylpyrrolidine; NAS, *N*-acryloylsuccinimide; NIPAM, *N*-isopropyl acrylamide; NMS, *N*-methacryloylsuccinimide; NPA, 4-nitrophenyl acrylate; NPMI, *N*-phenylmaleimide; NVCBz, *N*-vinylcarbazole; NVP, *N*-vinylpyrrolidone; NVI, *N*-vinylindole; ODA, octadecyl acrylate; ODAM, *N*-octadecyl acrylamide; PAA, propyl acrylic acid (2-methylenepentanoic acid); PAM, *N*-propylacrylamide; PhMA, phenyl methacrylate; PEO, poly(ethylene oxide) or poly(ethylene glycol); PFMA, pentafluorophenyl methacrylate; PEGA, ω -methyl[poly(ethylene glycol)] acrylate; PEGM, poly(ethylene glycol) monomethyl ether; PEGMA, ω -methyl[poly(ethylene glycol)] methacrylate; PLA, poly(lactic acid); PVK, phenyl vinyl ketone; RAFT, reversible addition–fragmentation chain transfer; S, styrene; SAC, 4-acetoxystyrene; SCl, 4- (or 3-)chlorostyrene; SMe, 4-methylstyrene; SCO₂H, styrene-4-carboxylic acid; SSO₃Na, sodium styrene-4-sulfonate; *t*-BA, *tert*-butyl acrylate; *t*-BAM, *N-tert*-butyl acrylamide; T, RAFT agent; TMAEMA, 2-(trimethylammonium)ethyl methacrylate; VAc, vinyl acetate; UV, ultraviolet; VBSC, vinylbenzenesulfonyl chloride; VBTAC, (4-vinylbenzyl)trimethylammonium chloride; VBz, vinyl benzoate; VDC, vinylidene chloride; VNd, vinyl neodecanoate; VPr, vinyl propionate; VSt, vinyl stearate; 2VP, 2-vinylpyridine; 4VP, 4-vinylpyridine; PMMA, poly(methyl methacrylate); PS, polystyrene. Abbreviations for polymers are formed by suffixing the abbreviation for the corresponding monomer with ‘P’. For example, PMMA – poly(methyl methacrylate), PS – polystyrene.

* Corresponding authors.

E-mail addresses: graeme.moad@csiro.au (G. Moad), ezio.rizzardo@csiro.au (E. Rizzardo), san.thang@csiro.au (S.H. Thang).

$$\phi = \frac{k_{\beta}}{k_{-\text{add}} + k_{\beta}} \quad (2)$$

The transfer constant is defined in terms of k_{tr} and the propagation rate constant (k_p) in the usual way ($C_{\text{tr}} = k_{\text{tr}}/k_p$).

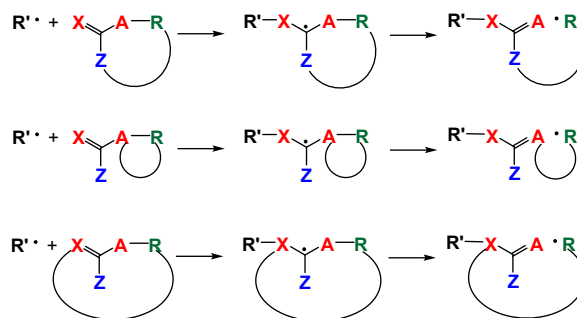
Efficient transfer requires that the radical intermediates formed by addition undergo facile β -scission (for **1**) or rearrangement (for **4**) to form a new radical that can reinitiate polymerization. The radical intermediates **2** and **5** typically have low reactivity towards further propagation and other intermolecular reactions because of steric crowding about the radical centre.

The driving force for fragmentation of the intermediate radical is provided by cleavage of a weak A–R or B–R bond and/or formation of a strong C=A bond (for **1**). If both addition and fragmentation are rapid and irreversible with respect to propagation the polymerization kinetics differ little from those seen in polymerization with conventional chain transfer. If the overall rate of β -scission is slow relative to propagation then retardation is a likely result. If fragmentation is slow, the adducts (**2** or **5**) also have a greater potential to undergo side reactions by addition to monomer (copolymerization of the transfer agent) or radical–radical termination. Retardation is often an issue with high k_p monomers such as VAc and MA. In designing transfer agents and choosing an R group, a balance must also be achieved between the leaving group ability of R and reinitiation efficiency of R^{\bullet} since, as with conventional chain transfer, the rate constant for reinitiation by R^{\bullet} should be $\geq k_p$. Factors discussed later with respect to RAFT agents are also important here. If fragmentation leads preferentially back to starting materials the transfer constants are low.

The methods used for evaluating transfer constants are the same as for conventional chain transfer and involve evaluating the molecular weight (as in Mayo method [20]) or the molecular weight distribution (as in the log CLD method [21,22]) in low conversion polymerizations or relative rate of consumption of transfer agent and monomer [23,24]. Transfer constants for addition–fragmentation chain transfer agents from the literature are summarized in the sections that follow.

When the product of the reaction is itself a potential transfer agent or a macromonomer, further reaction to form a block, graft or hyperbranched copolymer formation may occur particularly at high conversions [9,25]. The design of transfer agents that give reversible addition–fragmentation chain transfer (RAFT) has provided one of the more successful approaches to living radical polymerization and is described in the next section. The reverse pathway can also be blocked by choice of A. For example, when A is oxygen (e.g., vinyl ethers, Section 2.1, thionoesters, Section 2.4) or bears a substituent (e.g., A = CH–CH₃), the product is rendered essentially unreactive to radical addition.

If R and Z, R and A or, in principle, R and X in structure **1** are connected to form a ring structure the result is a potential ring-opening monomer as shown in Scheme 2. For many of the transfer agents described, there are analogous ring-opening monomers. Radical ring-opening polymerization has been reviewed by Moad and Solomon [26], Sanda and Endo [27],



Scheme 2. Potential propagation mechanisms in ring-opening polymerization.

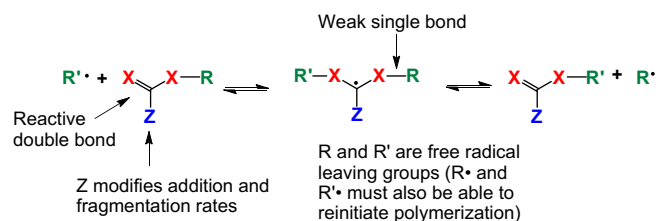
Klemm and Schulze [28], Cho [29], Moszner and Salz [30], Endo and Yokozawa [31], Stansbury [32] and Bailey [33].

1.2. Reversible addition–fragmentation chain transfer (RAFT)

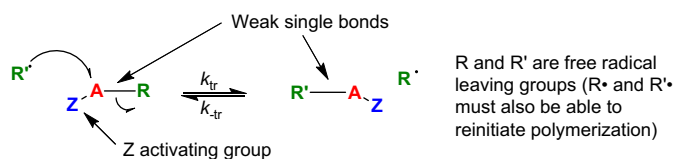
‘Macromonomers’ (**7**, X = CH₂; Scheme 3) have been known as potential reversible transfer agents in radical polymerization since the mid 1980s [9]. However, radical polymerizations which involve a ‘degenerate’ reversible chain transfer step for chain equilibration and which display at least some characteristics of living polymerization were not reported until 1995 [34,35].

Reversible chain transfer may, in principle, involve homolytic substitution (Scheme 4) or addition–fragmentation (RAFT) or some other transfer mechanism [36]. An essential feature is that the product of chain transfer is also a chain transfer agent with similar activity to the precursor transfer agent. The overall process has also been termed degenerate or degenerative chain transfer since the polymeric starting materials and products have equivalent properties and differ only in molecular weight (Scheme 3/Scheme 4, where R^{\bullet} and R'^{\bullet} are both propagating chains).

Polymerization of styrene and certain fluoro-monomers in the presence of alkyl iodides provided the first example of the reversible homolytic substitution process. This process is also known as iodine transfer polymerization [35,37]. Other



Scheme 3. Reversible addition–fragmentation chain transfer.



Scheme 4. Reversible homolytic substitution chain transfer.

more recent examples of control by reversible homolytic substitution chain transfer are polymerizations conducted in the presence of derivatives of organotellurides (TERP) [38] or organostibines [38] and tin, germanium or phosphorus iodides (RCTPs) [39].

In 1995 it was reported that polymerizations of methacrylic monomers in the presence of methacrylic macromonomers (7, $X = CH_2$, $Z = CO_2R$) under monomer-starved conditions display many of the characteristics of living polymerization [34,40]. These systems involve the RAFT mechanism (Scheme 5).

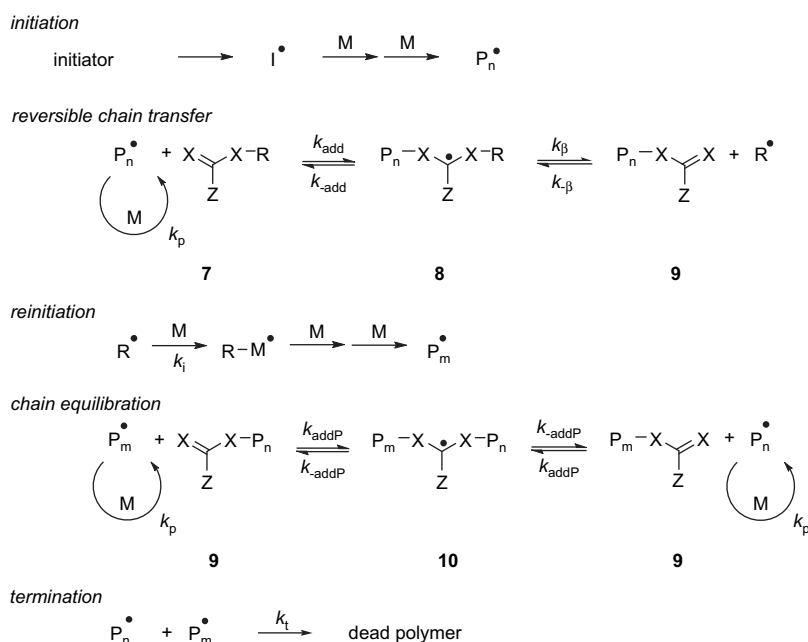
In 1982, Otsu et al. [41,42] proposed that living characteristics observed for polymerization in the presence of dithiocarbamate photoinitiators might be attributable to both reversible chain transfer and reversible radical–radical-coupling steps as part of the mechanism. However, it is now known that degenerate chain transfer is a minor pathway for the reagents and reaction conditions used in those pioneering experiments [43]. RAFT with thiocarbonylthio compounds (7, $X = S$) was first reported in 1998 [44,45] and is the most versatile and well-known process of this class [46,47]. It is compatible with most monomer types and with a very wide range of reaction conditions. Recent reviews which relate specifically to RAFT polymerization with thiocarbonylthio compounds include general reviews by Moad, Rizzardo and Thang [46–49], Mayadunne and Rizzardo [50], Chiefari and Rizzardo [14], Perrier and Takolpuckdee [51], Favier and Charreyre [52] and Barner-Kowollik, Davis, Stenzel and coworkers [53,54]. A book, entitled *Handbook of RAFT polymerization* [55] which comprises reviews on all aspects of RAFT polymerization has also just been published. Many other reviews deal with specific applications of RAFT polymerization such as computational studies related to RAFT agents and RAFT polymerization [56,57], the kinetics and mechanism of

RAFT polymerization [58,59], the control of molecular weight distributions produced by RAFT polymerization [60], RAFT polymerization in aqueous media [61,62], the use of RAFT polymerization in heterogeneous media [63–66], the synthesis of end-functional polymers by RAFT polymerization [67,68], star polymer synthesis [54,69], the synthesis and properties of stimuli responsive block and other polymers [68,70] and the preparation of honeycomb structures [71].

RAFT polymerization is also reviewed within works which deal more generically with radical polymerization. The literature through 2005 is comprehensively reviewed within the chapter *Living radical polymerization* in *The chemistry of radical polymerization* [72] and is given substantial coverage in many recent works that relate more generically to polymer synthesis, living polymerization or novel architectures [73–84]. Other relevant reviews include those focussing on the synthesis and organic chemistry of dithioesters and other thiocarbonylthio compounds in a non-polymerization context [85,86] and the use of RAFT in organic synthesis [87–89].

The literature is expanding very rapidly; an update review [47] covering the period mid 2005 to mid 2006 revealed >200 papers dealing directly with the use and application of RAFT polymerization. Our first communication on RAFT with thiocarbonylthio compounds [44] now has >1000 citations and is one of the most highly cited papers in *Macromolecules* and the first RAFT patent [45] was seventh on the list of most cited patents in the field of chemistry and related science in 2005 [90]. It should be noted that not all papers on RAFT polymerization cite these sources nor are all of the papers citing these documents specifically on RAFT polymerization.

The key feature of the mechanism of RAFT polymerization with thiocarbonylthio compounds as proposed in our first communication on the subject [44] is the sequence of addition–fragmentation equilibria shown in Scheme 5 [91]. Initiation



Scheme 5. Mechanism of RAFT polymerization.

and radical–radical termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical (P_n^*) to the thiocarbonylthio compound [$RSC(Z)=S$ (**7**)] followed by fragmentation of the intermediate radical provides a polymeric thiocarbonylthio compound [$P_nSC(Z)=S$ (**9**)] and a new radical (R^\bullet). Reaction of this radical (R^\bullet) with monomer forms a new propagating radical (P_m^*). Rapid equilibrium between the active propagating radicals (P_n^* and P_m^*) and the dormant polymeric thiocarbonylthio compounds (**9**) provides equal probability for all chains to grow and allows for the production of narrow polydispersity polymers. When the polymerization is complete (or stopped), the vast majority of chains retains the thiocarbonylthio end group and can be isolated as stable materials.

The reactions associated with RAFT equilibria shown in Scheme 5 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 effects 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 only 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.

For less active RAFT agents ($C_{tr} \leq 1$), transfer constants may be determined using the usual methods with little loss of accuracy. For more active transfer agents, where the transfer agent-derived radical (R^\bullet) may partition between adding to monomer and reacting with the polymeric RAFT agent (P_n^T) even at low conversions, the transfer constant measured according to the Mayo or related methods will appear to be dependent on the transfer agent concentration (and on the monomer conversion) [92–94]. This value should be called an apparent transfer constant C_{tr}^{app} and be regarded as a minimum value of the transfer constant. The actual transfer constant may be higher by several orders of magnitude [93]. The reverse transfer constant (C_{-tr}) is defined as follows (Eq. (3)):

$$C_{-tr} = \frac{k_{-tr}}{k_{iT}} \quad (3)$$

where k_{iT} is the rate of reinitiation by the RAFT agent-derived radical, R^\bullet , and the rate of transfer agent consumption is then given by Eq. (4):

$$\begin{aligned} \frac{d[T]}{d[M]} &\approx C_{tr} \frac{[T]}{[M] + C_{tr}[T] + C_{-tr}[P_n^T]} \\ &= C_{tr} \frac{[T]}{[M] + C_{tr}[T] + C_{-tr}([T_0] - [T])} \end{aligned} \quad (4)$$

This equation can be solved numerically to give estimates of C_{tr} and C_{-tr} [92,94].

The rate constant for the reverse transfer is defined analogously to that for the forward reaction (Eq. (1)) as shown in Eq. (5):

$$k_{-tr} = k_{-\beta} \frac{k_{-add}}{k_{-add} + k_{\beta}} \quad (5)$$

If the reverse reaction can be neglected Eq. (4) simplifies as follows:

$$\frac{d[M]}{d[T]} \approx C_{tr} \frac{[M]}{[T]} + 1 \quad (6)$$

which suggests that a plot of $\log(M)$ vs $\log(T)$ should be a straight line with the slope proving the transfer constant. This equation has been used to evaluate C_{tr} for a range of RAFT agents. For the more active RAFT agents, the values so obtained should be regarded as apparent transfer constants (C_{tr}^{app}) and as a minimum value for C_{tr} [92,93]. Values of C_{tr}^{app} and, where available, estimates of C_{tr} and C_{-tr} are included in tables in Section 3.

Systems that give reversible chain transfer can display the characteristics of living polymerization. Narrowed polydispersities will generally only be observed when $C_{tr} > 2$ and $C_{tr} > 10$ are required to achieve the characteristics often associated with living polymerization (i.e. significantly narrowed molecular weight distributions, molecular weights predictable from reagent concentrations that increase linearly with conversion). The more effective RAFT agents have $C_{tr} \gg 100$. The dependence of molecular weight and polydispersity on monomer conversion for various values of C_{tr} for a hypothetical polymerization without termination is shown in Fig. 1 [93]. Various factors will cause deviations from this ideal behavior (see, in particular, Section 3.3.3 below).

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 ($k_{add}, k_{-\beta}, k_{addP} \sim 10^6\text{--}10^8 \text{ M}^{-1} \text{ s}^{-1}$). Thus a high equilibrium constant generally implies a low fragmentation rate constant ($k_{-add}, k_{\beta}, k_{-addP}$) and consequently an increased likelihood for retardation and/or side reaction involving the adduct species. However, values of the equilibrium constants 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.

$K_P (= k_{addP}/k_{-addP})$ is associated with the chain equilibration process (Scheme 5). This step is sometimes called the main equilibrium.

$K (= k_{add}/k_{-add})$ and $K_{\beta} (= k_{-\beta}/k_{\beta})$ are associated with the initial reversible chain transfer step sometimes known as the pre-equilibrium.

$K_R (= k_{addR}/k_{-addR})$ is associated with the reaction of the expelled radical with the initial RAFT agent (Scheme 6). This process only becomes significant if the intermediate formed has a significant lifetime.

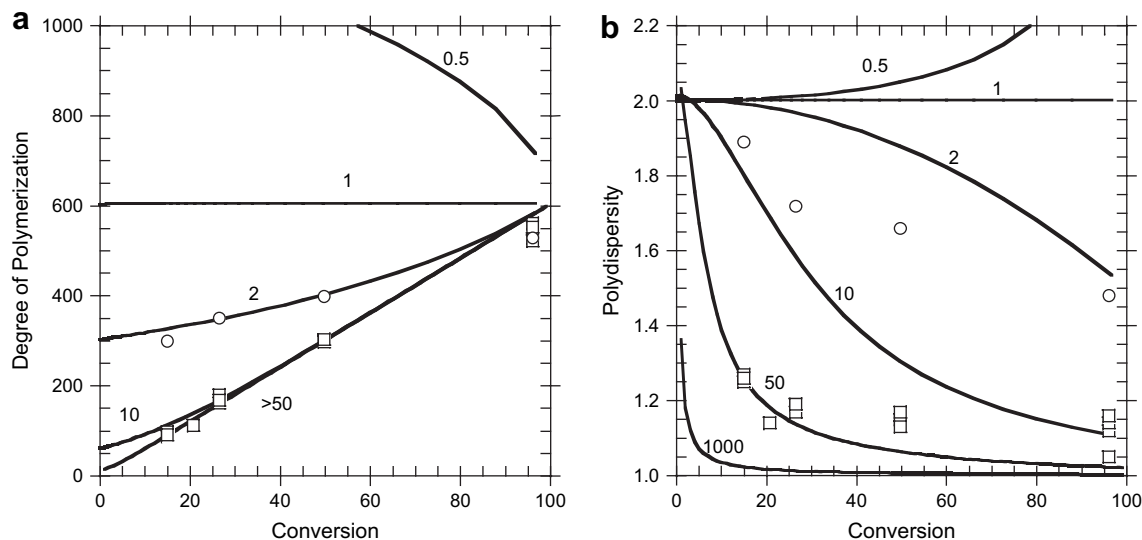
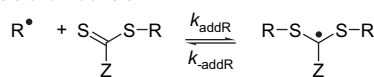


Fig. 1. Predicted dependence of (a) degree of polymerization and (b) polydispersity on conversion in polymerizations involving reversible chain transfer as a function of the chain transfer constant (C_{tr}). Predictions are based on equations proposed by Müller et al. [95,96] with $\alpha = 10^{-7}$ (the concentration of active species), β (the transfer constant) as indicated and $\gamma = 605$ (the ratio monomer to transfer agent). Experimental data points are for methyl methacrylate (7.02 M) polymerization in the presence of dithiobenzoate esters (0.0116 M) where $R = C(Me)_2CO_2Et$ (○) and $C(Me)_2Ph$ (□) (Figures reproduced from Ref. [93]. Copyright 2003 American Chemical Society).

reversible chain transfer



Scheme 6.

There may be other equilibrium constants to consider if penultimate group effects are significant (there is theoretical data [97,98] and some experimental evidence [93,99] to indicate 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.

It should be possible to estimate values of K by determining the concentrations of the radical intermediates in RAFT polymerization by EPR (or ESR) spectrometry and some effort has been directed to this end [100–103]. Coote and coworkers [56,97,98,104–107] 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 [108–110]. Values of K estimated on the basis of the measured concentrations of the radical

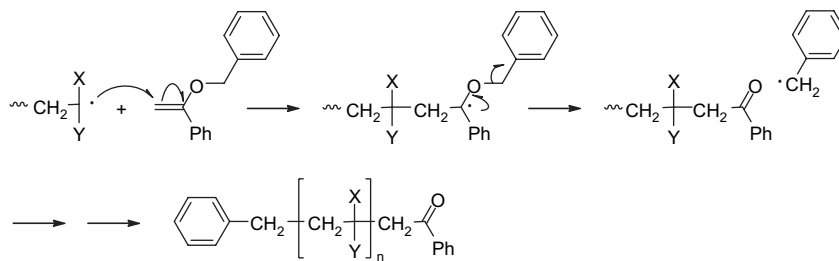
intermediates are substantially lower than those predicted by theoretical calculations.

2. Compounds providing irreversible addition–fragmentation chain transfer

2.1. Vinyl ethers

2.1.1. Addition–fragmentation chain transfer agents

The vinyl ethers (**1**, $X = CH_2$, $A = O$) can be very effective addition–fragmentation chain transfer agents [7,11,111,112]. The mechanism for chain transfer is shown in Scheme 7 for the case of α -benzyloxystyrene (**16**). The driving force for fragmentation is provided by formation of a strong carbonyl double bond. It is also important that R is a good radical leaving group. The vinyl carbonate **13** [112] gives only copolymerization, the ketene acetal **11** [113] and the methyl vinyl ether **14** [112] give both copolymerization and chain transfer in styrene polymerization whereas with the benzyl vinyl ethers, **12** [113], **16** [7] and **17–19** [111], chain transfer is the only reaction detected. Transfer constants for some vinyl ether transfer agents are provided in Table 1. The examples with an $R = \text{benzyl}$ are



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Scheme 7.

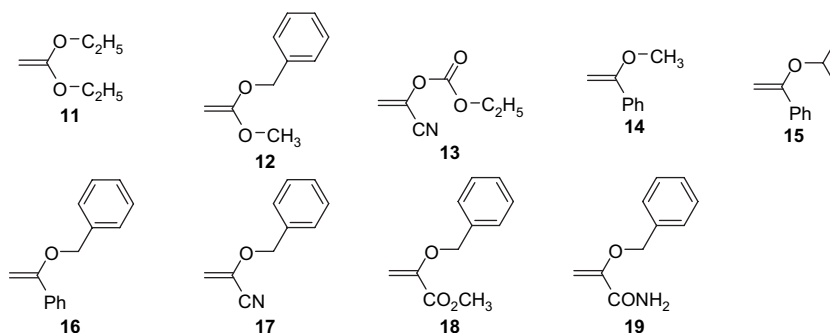


Table 1
Transfer constants for vinyl ethers at 60 °C^a [17]

Transfer agent	C_{tr} for monomer				References
	S	MMA	MA	VAc	
14	–	0.02	–	–	[116]
15	–	0.25	–	–	[116]
16	0.26	0.76	5.7 ^b	9.7 ^b	[7,111]
17	0.036	0.081	0.3 ^b	12 ^b	[111]
18	0.046	0.16	0.54 ^b	20 ^b	[111]
19	0.2	0.5	1.1 ^b	–	[111]

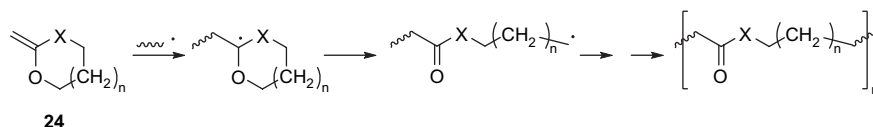
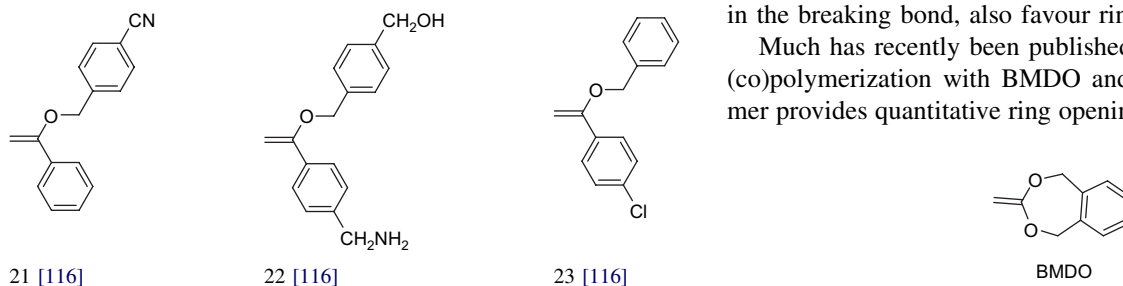
^a Bulk medium comprises only monomer and transfer agent.

^b Significant retardation observed.

appropriate for use in S or (meth)acrylate ester polymerization but give retardation in polymerization of VAc and related monomers because benzyl radical is slow to initiate these polymerizations. Reagents **1** with X = CH₂, A = O, R = tertiary alkyl or cyclopropylcarbinyl have been shown to be effective as addition–fragmentation transfer agents in organic synthesis but have not been used in polymerization [114,115].

The polymers formed have a ketone end group (e.g., **20**, Scheme 7). Additional functionality can be introduced on ‘Z’ or ‘R’ to modify reactivity or to tailor the end groups as in the examples (**21–23**) [11].

The vinyl ether transfer agents, like other vinyl ethers, generally show marked acid sensitivity and are not suited for use with acidic monomers (e.g., AA, MAA). Even traces of acidic impurities in the monomer or the polymerization medium can catalyze decomposition of the transfer agent.



Scheme 8.

2.1.2. Ring-opening monomers

The ring-opening polymerization of ketene acetals (**24**, X = O) provides a route to polyesters by radical polymerization and many examples have been reported (Scheme 8) [117–121]. A disadvantage of these systems is the marked acid sensitivity of the monomers which makes them relatively difficult to handle and complicates characterization. The early literature in this area is covered by a series of reviews by Bailey et al. [33,122–126] and an updated summary has been provided by Moad and Solomon [26].

The nitrogen (**24**, X = N–CH₃, $n = 0$) [127] and sulfur (**24**, X = S, $n = 0$) [128] analogues of ketene acetals undergo ring-opening polymerization with selective cleavage of the C–O bond to give polyamides or polythioesters, respectively (Scheme 8). The specificity is most likely a reflection of the greater bond strength of C=O vs the C=S or C=N double bonds. The corresponding dithianes do not give ring opening even though this would involve cleavage of a weaker C–S bond [129,130].

The competition between ring opening and propagation is dependent on ring size and substitution pattern. For the five-membered ring ketene acetal (**24**, X = O, $n = 0$) ring opening is not complete except at very high temperatures. However, with the larger-ring system (**24**, X = O, $n = 2$) ring opening is quantitative. This observation (for the $n = 2$ system) was originally attributed to greater ring strain. However, it may also reflect the greater ease with which the larger-ring systems can accommodate the stereoelectronic requirements for β -scission [131]. β -Substituents (e.g., CH₃, Ph) which lend stabilization to the new radical centre, or which increase strain in the breaking bond, also favour ring opening.

Much has recently been published on radical ring-opening (co)polymerization with BMDO and derivatives. The monomer provides quantitative ring opening, copolymerizes readily

with styrenic and acrylic monomers [132–141] and is compatible with RAFT [142] and ATRP [135,138,140,141].

2.2. Allyl sulfides, sulfones, halides, phosphonates, silanes

2.2.1. Addition–fragmentation chain transfer agents

Allyl transfer agents (**1**, X = CH₂, A = CH₂) include allyl sulfides (e.g., **25**, **27–34**) (Table 2) [8,143,144], allyl sulfones (e.g., **35–41**) [145] and sulfoxides (e.g., **42**) (Table 3) [145,146], and allyl halides (e.g., **43–45**) [145,147–152], phosphonates (e.g., **46**) [145], silanes (e.g., **48**) [145] and related compounds (Table 4). Rates of addition are determined by the activating group 'Z' as discussed above. The low transfer constant of **32** in styrene polymerization demonstrates the importance of choosing 'Z' to suit the particular monomer. The main driving force for fragmentation is the weak single A–R bond of **2**. In many cases the chain transfer constants are close to the 'ideal' value of unity.

The mechanism of chain transfer is shown in Scheme 9 for allyl sulfide **25**. The product, macromonomer (**26**), may undergo further reaction under the polymerization conditions particularly at high conversion (Section 3).

Allyl bromides **43a**, **44**, and **45a** give predominantly chain transfer whereas, the chlorides (e.g., **45b**) give copolymerization

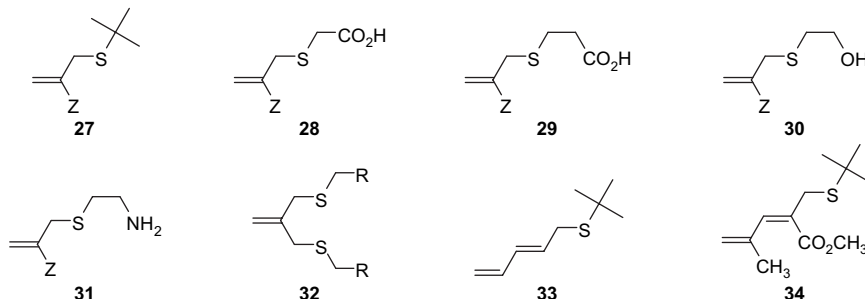
as well as chain transfer [145,158]. The silane **48** also gives copolymerization as well as chain transfer [145]. Allyl ethers (**1**, R = alkoxy, X = A = CH₂) are generally not addition–fragmentation chain transfer agents but are comonomers and may give degradative chain transfer by hydrogen abstraction.

2.2.2. Ring-opening monomers

Cyclic allyl sulfide derivatives (**52–57**) are stable in storage and handling and do not show the acid sensitivity of the cyclic ketene acetal monomers mentioned above. The monomers with seven- and eight-membered rings undergo facile polymerization even at relatively low temperatures [161–169] with quantitative ring opening (Schemes 10 and 11). The monomers also undergo facile ring-opening copolymerization with MMA and S [165,166]. The corresponding six-membered ring compound (**52**) appears unreactive in homopolymerization.

Ring opening provides a thiyl radical propagating species. Although the polymers have a double bond on the backbone it is possible to conduct polymerization such that there is little or no crosslinking. There is, however, evidence of reversible addition and addition–fragmentation involving this double bond [167]. Monomers containing multiple double bonds have been designed to provide ring-opening polymerization with crosslinking [163].

Table 2
Transfer constants for allyl sulfides at 60 °C^a (data taken from Ref. [17])



Transfer agent	C _{tr} for monomer				
	S	MMA	MA	MAN	VAc
27 , Z = Ph	0.80 [8]	1.2 [8]	3.9 ^b [11]	–	~20 ^b
27 , Z = CN	1.90 [8]	1.35 [8]	1.6 ^b [11]	–	~60 ^b
27 , Z = CO ₂ Et	0.95 [8]	0.74 [8]	2.2 ^b [11]	0.42 [153,154]	~27 ^b [154]
28 , Z = Ph	0.95 [143]	1.1 [143]	–	–	–
28 , Z = CO ₂ Et	1.72 [143]	0.65 [143]	–	–	–
28 , Z = CO ₂ H	1.27 [143]	0.74 [143]	–	–	–
29 , Z = Ph	0.68 [143]	–	–	–	–
30 , Z = Ph	0.77 [143]	1.04 [143]	–	–	–
30 , Z = CO ₂ H	1.81 [143]	0.27 [143]	1.49 ^c [143]	–	–
30 , Z = CO ₂ CH ₂ CH ₂ OH	0.77 [143]	0.40 [143]	1.88 ^c [143]	–	–
31 , Z = Ph	0.79 [143]	0.91 [143]	–	–	–
32 , R = CH ₂ CO ₂ CH ₃ ^d	0.016 [155]	–	–	–	–
33	0.35 [156]	1.11 [156]	–	–	–
34	1.51 ^d [157]	0.33 ^d [157]	–	–	–

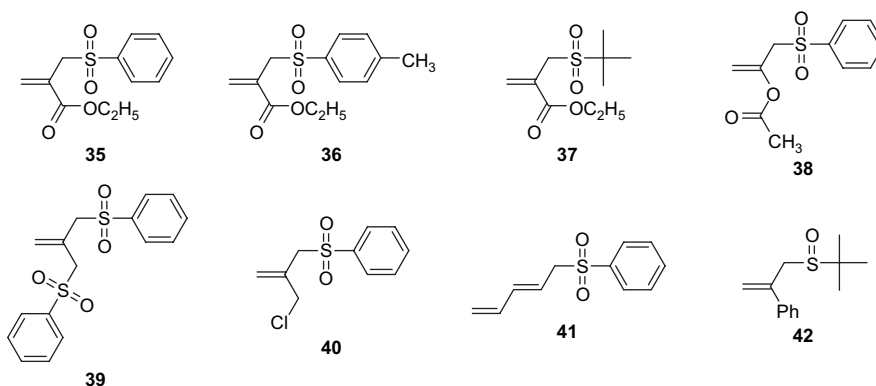
^a Bulk polymerization.

^b Significant retardation observed.

^c BA.

^d Transfer constants similar for various R.

Table 3
Transfer constants for allyl sulfones and allyl sulfoxides at 60 °C^a (data taken from Ref. [17])



Transfer agent	C_{tr} for monomer ^b				References
	S	MMA	BA	VAc	
35	4.2 ^d	0.72 ^d	1.1 ^d	— ^c	[146]
36	5.8	1.1	2.3 ^d	— ^c	[145]
37	—	1.0	—	—	[145]
38	0.02	0.065	0.20 ^e	2.8	[145]
39	—	—	—	3.9	[14]
40	—	—	—	0.05	[14]
41	—	3.0	—	—	[159]
42	—	1.9	—	—	[145]

^a Bulk medium comprises only monomer and transfer agent.

^b Transfer constants rounded to two significant figures.

^c Significant retardation observed.

^d 3.46 M monomer in benzene solution [146].

^e MA.

	52 [164]		53 [161,168]
	54a R = H [162] b R = CH ₃ [164] c R = CH ₂ O(C=O)CH ₃ [163,164] d R = CH ₂ O(C=O)C(CH ₃)=CH ₂ [163]		55a R = H [161,168] b R = CH ₃ [161]
	56a R ¹ , R ² , R ³ , R ⁴ = H [162] b R ¹ , R ² , R ³ = H; R ⁴ = CH ₃ [164,167,169] c R ¹ , R ³ , R ⁴ = H; R ² = O(C=O)CH ₃ [163,164] d R ¹ , R ³ , R ⁴ = H; R ² = O(C=O)Ph [163] e R ¹ = H; R ² , R ³ , R ⁴ = CH ₃ [166,169]		57 [168]

2.3. Allyl peroxides

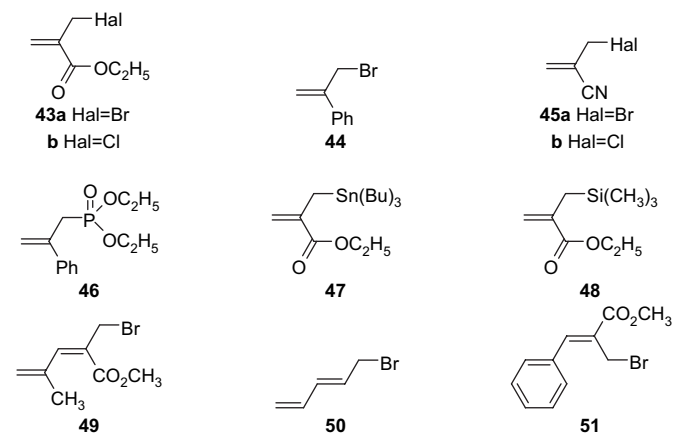
In the case of allyl peroxides (**4**, X = CH₂, A = CH₂, B = O, R = *O*-alkyl) [170–174], intramolecular homolytic substitution on the O–O bond gives an epoxy end group as shown in Scheme 12 (1,3-S_Hi mechanism). The allyl peroxides usually are thermally stable under the conditions used to determine their chain transfer activity and conditions typically used in polymerizations. They may, however, be thermally unstable at higher temperatures. The transfer constants are more than two orders of magnitude higher than those for dialkyl peroxides such as di-*tert*-butyl peroxide

($C_1 = 0.00023$ – 0.0013) or di-isopropyl peroxide ($C_1 = 0.0003$) which are believed to give chain transfer by direct attack on the O–O bond [175] (Table 5). This is circumstantial evidence in favour of the addition–fragmentation mechanism.

Peroxyacetals **64** [176] and peresters such as **67** [177] can also be effective transfer agents. However, at typical polymerization temperatures (~60 °C) they are thermally unstable and also act as initiators. Compounds such as **68** which may give addition and 1,5-intramolecular substitution with fragmentation have also been examined for their potential as chain transfer agents (1,5-S_Hi mechanism) [180].

Table 4

Transfer constants for allyl halides, phosphonates, silanes and stannanes at 60 °C^a (data taken from Ref. [17])



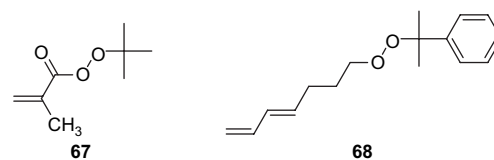
Transfer agent	C_{tr} for monomer ^b				References
	S	MMA	MA	VAc	
43a, Hal = Br	—	1.5	2.3	—	[145]
44	2.9	2.3	5.3	—	[145]
45a, Hal = Br	—	2.2	3.0	—	[145]
45b, Hal = Cl	—	0.0075 ^d	0.046 ^d	—	[145]
46	—	0.4	—	—	[145]
47	—	3.0	—	—	[145]
48	—	0.08 ^d	—	—	[145]
49	—	3.4	—	—	[159]
50	8.1	7.4 ^c	—	—	[159]
51	0.25	—	—	—	[160]

^a Bulk medium comprises only monomer and transfer agent.

^b Transfer constants rounded to two significant figures.

^c Significant retardation observed.

^d Copolymerization observed.



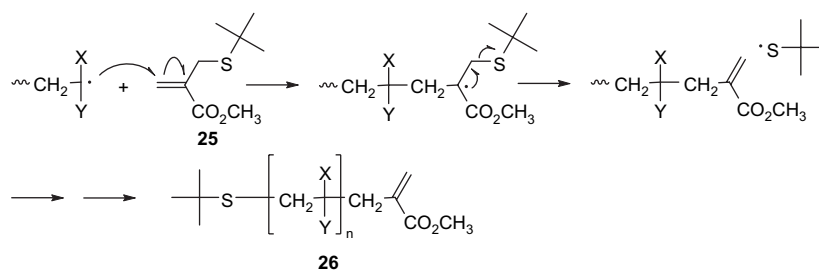
2.4. Thionoester and related transfer agents

Thione derivatives (e.g., **69–71**, Table 6) [181–183] also are very effective as addition–fragmentation chain transfer agents.

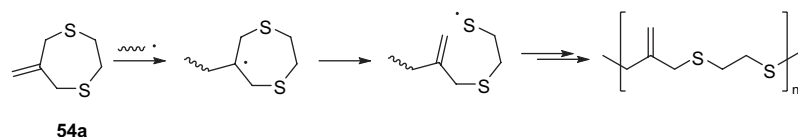
The thiohydroxamic esters (e.g., **70**) are sometimes known as Barton esters because of the work of Barton and coworkers who explored their use in organic synthesis [184–186]. When the initiating species formed are acyloxy radicals they may undergo decarboxylation before initiating a new chain. Thus for the example shown in Scheme 13, products with benzoyloxy and phenyl chain ends are expected (**72** and **73**, respectively).

Benzyl thionobenzoate (**69**) is believed to be ineffective as a transfer agent in MMA polymerization because of an unfavorable partition coefficient. PMMA• is a much better radical leaving group than benzyl radical. Analogous benzyl thiocarbonylthio compounds are also ineffective as RAFT agents in MMA polymerization.

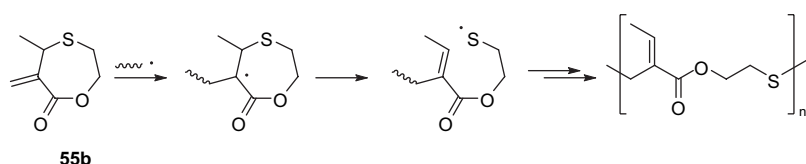
Thiohydroxamic esters have also seen application in grafting of PAN onto PE [187], of PS, PAM and PNIPAM onto cellulose [188,189] and of PS, PMMA, PVP and PAM onto poly(arylene ether sulfone) [190]. The process involves derivatization of a parent carboxy functional polymer to form the thiohydroxamic ester **70** with R = polymer, which then behaves as a polymeric transfer agent.



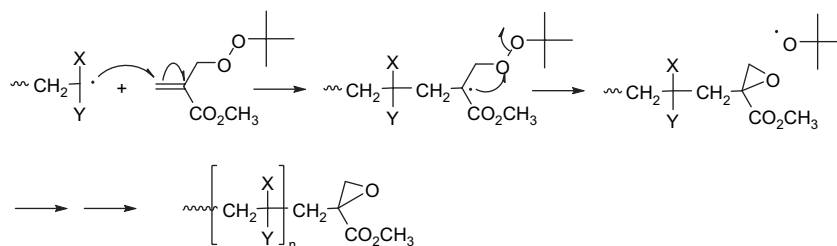
Scheme 9.



Scheme 10. See Ref. [162].



Scheme 11. See Ref. [161].



Scheme 12.

3. Compounds providing reversible addition–fragmentation chain transfer

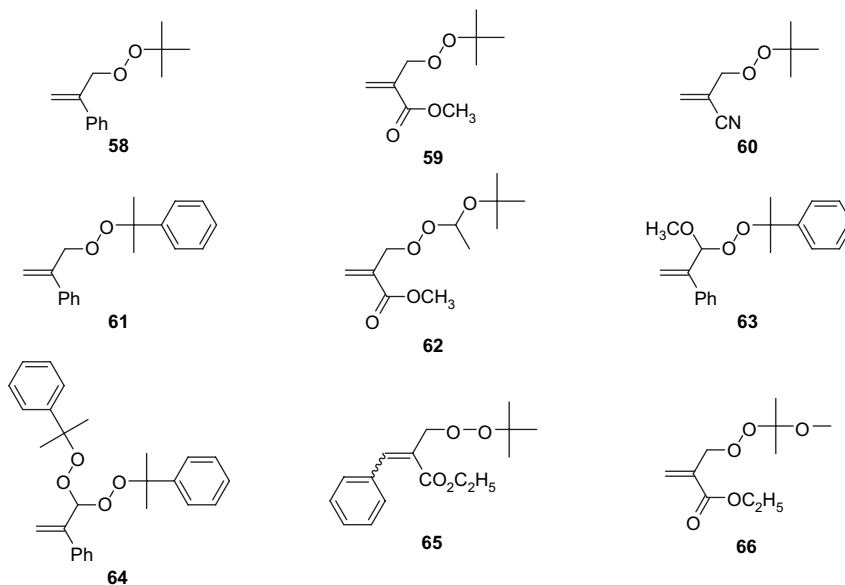
A wide variety of macromonomer (7, X = CH₂) and thiocarbonylthio RAFT agents (7, X = S) have now been reported. The effectiveness of RAFT agent depends on the monomer being polymerized and depends strongly on the properties of the radical leaving group R and the group Z which can be chosen to activate or deactivate

the thiocarbonyl double bond and to modify the stability of the intermediate radicals. For an efficient RAFT polymerization [46]:

- the RAFT agents (7) and (9) should have a reactive C=X double bond (high k_{add}).
- The intermediate radicals (8) and (10) should fragment rapidly (high k_{β} , weak X–R bonds) and give no side reactions.

Table 5

Transfer constants for allyl peroxide and related transfer agents at 60 °C^a (data taken from Ref. [17])



Transfer agent	C_{tr} for monomer ^b				References
	S	MMA	MA	VAc	
58	0.9	0.8	–	–	[11,170]
59	1.6	0.6	1.0	–	[11,170]
60	2.0	0.9	0.7	–	[11]
61	0.8	0.8	–	–	[11,170]
61	0.66	–	–	–	[171]
63	0.92	0.49	1.9	–	[176]
64	0.9	–	–	–	[176]
65	0.22	0.012	0.08	3.7	[160]
67	0.82 ^b	0.31 ^b	–	–	[177]
66	0.35 ^c	0.05 ^c	0.46 ^{c,d}	1.3 ^c	[178,179]
68	0.14	0.57	1.31 ^d	–	[180]

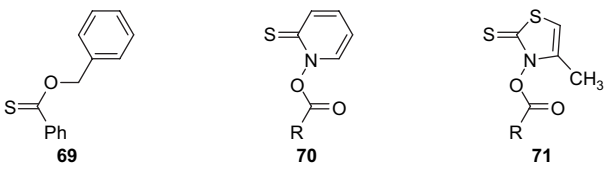
^a Bulk medium comprises only monomer and transfer agent.

^b Compound is also an initiator under the polymerization conditions. Transfer constant obtained using a modified Mayo equation [177].

^c In benzene.

^d BA.

Table 6
Transfer constants for thionoester and related transfer agents at 60 °C^a (data taken from Ref. [17])



Transfer agent	C_{tr} for monomer				References
	S	MMA	MA	VAc	
69	1.0	~0	1.2 ^b	>20 ^c	[183]
70 , R = C ₁₅ H ₃₁	3.8	4.0	~20 ^b	~36 ^c	[182]
70 , R = PhCH ₂	3.9	4.3	—	~80 ^c	[182]
70 , R = Ph	—	2.8	—	—	[182]
71 , R = C ₁₅ H ₃₁	0.3	0.6	3.1	9.7 ^b	[182]
71 , R = PhCH ₂	1.0	1.0	—	18 ^c	[182]

^a Bulk medium comprises only monomer and transfer agent.

^b Significant retardation observed.

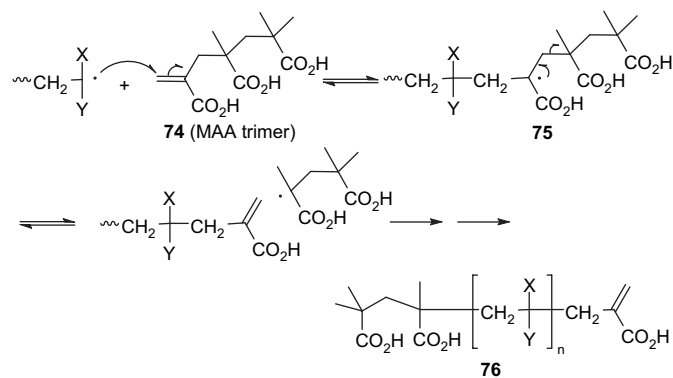
^c Strong retardation observed.

- The intermediate (**8**) should partition in favour of products ($k_{\beta} \geq k_{-add}$).
- The expelled radicals (R•) should efficiently reinitiate polymerization.

3.1. Macromonomers

Macromonomers (**7**, X = CH₂, R = polymer chain) can react by a RAFT mechanism as shown in Scheme 14 for ‘MAA trimer’ (**74**) [9,25]. The product (**76**) is also a ‘macromonomer’ thus chain transfer is reversible and ‘degenerate’ [34,40]. These chain transfer agents are frequently called ‘macromonomers’ even when used as transfer agents. This may appear to be a misnomer, since when used in this context, they should not behave as macromonomers. Copolymerization when it occurs is a side reaction. The most reported transfer agents of this class are the methacrylate macromonomers (e.g., **77–79**) and AMS dimer (**89**).

Methacrylic macromonomers are conveniently synthesized by catalytic chain transfer [191]. They can also be synthesized by polymerizations in the presence of other addition–fragmentation chain transfer agents (**1**) with X = A = CH₂ described in Section 2. The macromonomer chain end is also

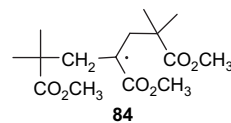


Scheme 14.

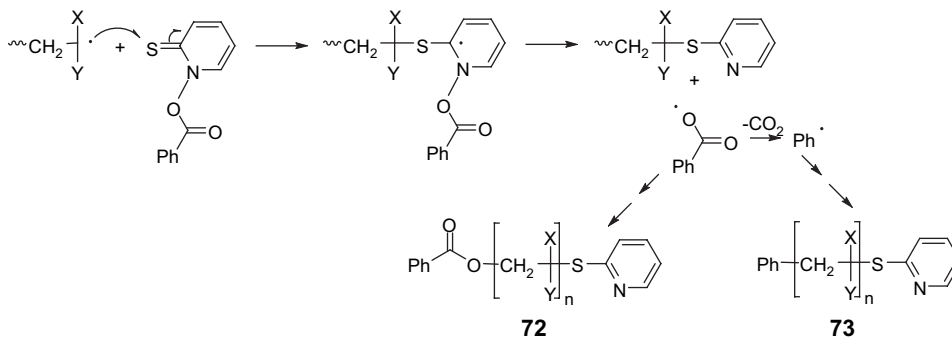
identical in structure to the unsaturated chain end formed by termination by disproportionation [192].

Transfer constants for selected macromonomers are tabulated in Table 7. The rate constants (k_{add}) for addition of the MMA propagating radical [19] (and other radicals [25]) to macromonomers (e.g., **77–79**) are believed to be essentially independent of the macromonomer chain length (n). However, the rate constants for addition and fragmentation are subject to significant penultimate unit effects and are dependent on the chain length of the propagating radical for $n < 5$. This is attributed to steric factors [19,24]. One consequence is that the transfer constant of ‘dimer’ (**77**) is more than an order of magnitude lower than that for ‘trimer’ (**78**) and higher macromonomers **79** due to an unfavorable partition coefficient. Fragmentation of **83** preferentially gives back **77** and the MMA propagating radical (**80**) rather than **81** and the monomeric radical (**82**) (Scheme 15).

The observation by Tanaka et al. [192] that the adduct **84** from the monomeric MMA radicals adding to ‘MMA dimer’ is persistent while higher adducts **83** are transient (lifetime too short to be observable by ESR) may be seen as a further consequence of a penultimate unit effect [19].

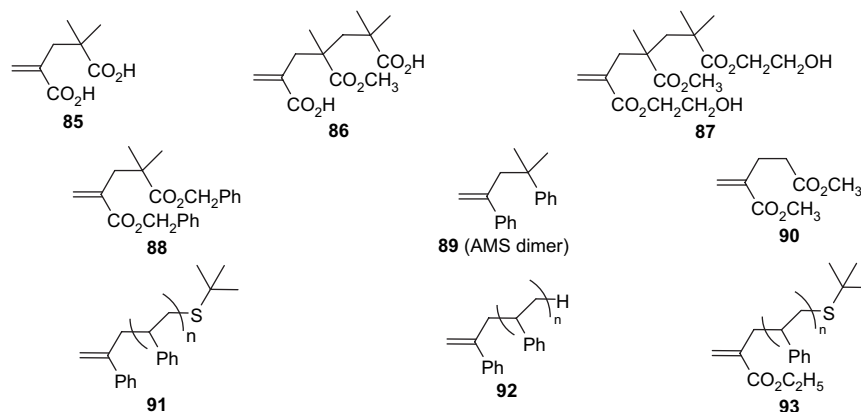


Transfer constants of the methacrylate macromonomers in MMA polymerization appear independent of the ester group. Those for MAA dimer and trimer are slightly higher than

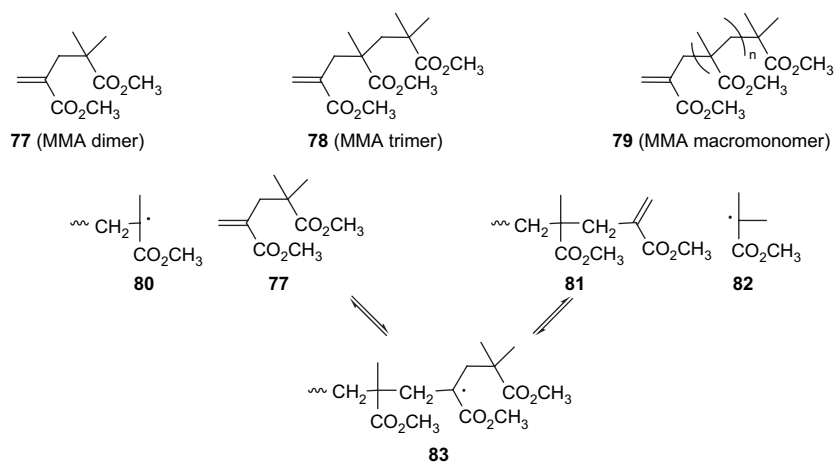


Scheme 13.

Table 7

Transfer constants for macromonomers (data taken from Ref. [17])^a

Transfer agent	T (°C)	C_{tr} for monomer ^b			References
		S	MMA	EA	
77 (MMA dimer)	60	—	0.013	0.12 ^d	[19,193]
78 (MMA trimer)	60	0.55 ^d	0.19	0.84 ^d	[19,193]
79, $n = 2$	60	—	0.31	—	[19]
79, av. $n = 14$	60	—	0.21	—	[19]
85 (MAA dimer)	60	—	0.18	—	[24]
74 (MAA trimer)	60	—	0.26	—	[24]
86	60	—	0.18	—	[24]
87	60	—	0.27	—	[24]
88	60	—	0.015	—	[194]
89 (AMS dimer)	60	0.24	0.09 ^f	—	[195]
89 (AMS dimer)	110	0.28	0.13	—	[16,195,196]
91	120	0.16	—	—	[195]
92	120	0.11	—	—	[195]
93	120	0.15	0.14 ^f	—	[195]
96	60	0.552 ^{c,d}	0.123 ^{c,d}	—	[197]
97	60	0.004	0.004	0.02 ^c	[198]
98	60	0.15	0.015	0.20	[198]
99	60	—	0.06	0.45	[198]

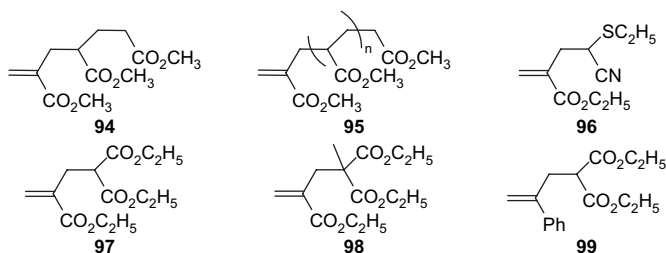
^a Bulk medium comprises only monomer and transfer agent.^b All transfer constants rounded to two significant figures.^c Significant retardation observed.^d Copolymerization observed as side reaction.^e MA, 80 °C.^f BMA.

Scheme 15.

for the corresponding esters. End-functional trimers **86** and **87** can be synthesized from the MMA trimer (**78**) by selective hydrolysis or hydrolysis and reesterification, respectively, and offer a route to telechelic polymers [24].

In polymerization of monosubstituted monomers (e.g., S, BA), copolymerization of the macromonomer to form a graft copolymer is invariably a significant pathway [9]. Fragmentation is favoured by elevated reaction temperatures [40].

For polymerization of MMA in the presence of the macromonomers **90** [199], **94** [200] and **95** [201], where the leaving group is a primary or secondary radical, the adduct radical partitions between fragmentation and propagation. In the case of **96**, where the leaving group is a more stable radical, fragmentation becomes the favoured pathway but copolymerization is still observed [197]. The intermediate formed by polymerization of monosubstituted monomers in the presence of a ‘trimer’ such as **94** is similar to that produced by backbiting β -scission during polymerization [202].



Because transfer constants of the macromonomers are typically low (<0.5) it is necessary to use starved–feed

conditions to take full advantage of RAFT, achieve low dispersities and make block copolymers. Best results have been achieved using emulsion polymerization [34,40] where rates of termination are lowered by compartmentalization effects. A ‘one-pot’ process where macromonomers were made *in situ* by catalytic chain transfer was developed [34,40]. Molecular weights up to 28,000 that increase linearly with conversion as predicted, molecular weight distributions that narrow with conversion down to $\overline{M}_w/\overline{M}_n < 1.3$ and block purities $>90\%$ can be achieved [34,40]. Surfactant-free emulsion polymerizations are made possible by use of an MAA macromonomer as the initial RAFT agent to create ‘self-stabilizing lattices’. Some examples of block copolymers synthesized by macromonomer RAFT polymerization are provided in Table 8 [203].

3.2. Thiocarbonylthio compounds

Thiocarbonylthio RAFT agents include certain dithioesters, trithiocarbonates, xanthates, dithiocarbamates and other compounds. Fig. 2 provides general guidance on how to select the appropriate thiocarbonylthio RAFT agent for a particular monomer. It should be clear that with just two RAFT agents it should be possible to exert effective control over the vast majority of polymerizations. For example a tertiary cyanoalkyl trithiocarbonate (e.g., **195**, **196**) provides excellent control and no or little retardation in RAFT polymerizations of (meth)acrylates, (meth)acrylamides and styrene. A cyanoalkyl

Table 8
Block copolymers prepared by macromonomer RAFT polymerization under starved–feed conditions [34,40]

Macro ^a	\overline{M}_n	$\frac{\overline{M}_w}{\overline{M}_n}$	Monomer	Solvent	T (°C)	\overline{M}_n	$\frac{\overline{M}_w}{\overline{M}_n}$
MAA	950	—	MMA	Emulsion	80	3000	1.4
MMA	3500	1.6	BMA	Emulsion	80	28,000	1.4
MMA	2050	1.7	EHMA	Emulsion	80	11,800	1.3
<i>t</i> -BMA	2400	2.1	BMA	Emulsion	80	5800	1.3
PhMA	1100	2.2	BMA	Emulsion	80	14,500	2.3
HEMA	1550	—	MMA	H ₂ O/ <i>i</i> -PrOH	80	3600	1.8
BMA	1050	2.0	S	BuAc	125	4700	2.4 ^b
MMA–MAA	1030	1.5	BA	BuAc	125	2700	1.8 ^c

^a Macromonomer made from monomer shown by catalytic chain transfer [34,40].

^b After subtraction of residual macromonomer.

^c Contains graft copolymer impurity.

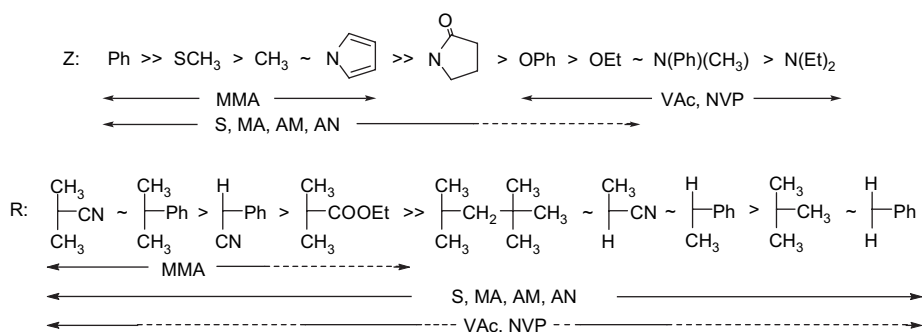


Fig. 2. Guidelines for selection of RAFT agents for various polymerizations [46,47,204]. For Z, addition rates decrease and fragmentation rates increase from left to right. For R, fragmentation rates decrease from left to right. Dashed line indicates partial control (i.e. control of molecular weight but poor polydispersity or substantial retardation in the case of VAc).

dithiocarbamate (e.g., **257**) or xanthate (e.g., **290**) enables similar control over RAFT polymerizations of vinyl acetate, vinyl pyrrolidone and similar monomers. Other RAFT agents may be required for solubility or compatibility with particular polymerization media or to provide specific end group functionality. The use of bis- and multi-RAFT agents (see Section 3.4.5) permits the synthesis of polymers with complex architectures. Symmetrical trithiocarbonates can also be considered as a member of the class of bis-RAFT agents.

A summary of RAFT agents that have been prepared and the polymerizations in which they have been applied can be found in the following sections (Sections 3.2.1–3.2.5). Monomer/RAFT agent combinations that have proved ineffective or which are less effective are indicated by the monomer being in parentheses. The criteria for effectiveness are (a) that there is polymerization, (b) that the molecular weight should be controlled and (c) that polydispersity obtained should be less than or equal to 1.4 under the conditions reported. There is some subjectiveness in these criteria since the level of control is dependent on polymerization conditions. It should be pointed out that a broad molecular weight distribution is not by itself an indication that there is a low fraction of living chains and thus it should not be taken as an indication that the RAFT agent is not useful for preparing block copolymers or for preparing end-functional polymers based on the indicated monomer.

A more quantitative indication of effectiveness is provided by the transfer constant data (Table 9 – dithioesters, Table 14 – trithiocarbonates, Table 21 – dithiocarbamates and xanthates). However, such data are, as yet, available for few systems. Moreover, most reported transfer constants (even when not

indicated as such) are ‘apparent transfer constants’ (C_{tr}^{app} , see discussion above) and care should be taken when using these data to extrapolate to polymerization conditions different to those under which the data were obtained.

3.2.1. Dithioesters

A wide range of dithioester RAFT agents have been reported. A summary of mono RAFT agents and their application are provided in Table 10 (Z = aryl) and Table 13 (Z = alkyl or aralkyl). Examples of unprotected functionality that have been incorporated into the ‘R’ fragment of dithiobenzoate RAFT agents include hydroxy (**117**), carboxylic acid/carboxylate (**110**, **125**, **145**, **149**, **191**) sulfonic acid/sulfonate (**119**, **137**), azide (**113**), olefin (**114**, **115**, **116**) and siloxane (**135**). Bis- and multi-dithioester RAFT agents that may be used for triblock or star synthesis are summarized in Tables 11 and 12, respectively. Bis-dithioesters can be used to synthesize triblock copolymers in a two-step process.

Dithiobenzoates and similar dithioesters with Z = aryl are amongst the most active RAFT agents and with appropriate choice of ‘R’ have general applicability in the polymerization of (meth)acrylic and styrenic monomers [46,47]. However, their use can give retardation, particularly when used in high concentrations (to provide lower molecular weight polymers) and with high k_p monomers (acrylates, acrylamides). They are also more sensitive to hydrolysis and decomposition by Lewis acids [204] than other RAFT agents.

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*

Table 9
Transfer and rate coefficients for dithioester RAFT agents

Agent	Z	R	Monomer	T (°C)	C_{tr}^{app}	C_{tr}	C_{-tr}	k_{add} ($10^{-6} \times M^{-1} s^{-1}$)	ϕ	References
100	Ph	PMMA	MMA	60 ^a	140	140	140	–	0.5	[211]
101	CH ₃	PMMA	MMA	40	40	40	40	–	0.5	[99]
103	CH ₃	PS	MMA	40	0.83	–	–	–	–	[99]
104a	Ph	C(CH ₃) ₂ Ph	MMA	60	5.9	56 ^b	2500 ^b	–	–	[93]
106a	Ph	C(CH ₃) ₂ CN	MMA	60	6.8	25 ^b	450 ^{d,b}	–	–	[93]
120b	Ph	C(CH ₃) ₂ E ^c	MMA	60	1.7	–	–	–	–	[92]
144a	Ph	CH ₂ Ph	MMA	60	<0.03	–	–	–	–	[93]
190	PhCH ₂	CH(CH ₃)E ^c	MA	60	93 ^d	–	–	1.3	0.5	[212]
144a	Ph	CH ₂ Ph	MA	60	105	–	–	–	–	[93]
123	Ph	<i>t</i> -C ₄ H ₉	BA	60	100	–	–	–	–	[213]
102	Ph	PS	Styrene	60	~6000	~6000	~6000	~2	0.5	[211]
103	CH ₃	PS	Styrene	60 ^a	180	180	180	0.05	0.5	[211]
103	CH ₃	PS	Styrene	40	220	220	220	–	0.5	[99]
101	CH ₃	PMMA	Styrene	40	420	–	–	–	–	[99]
104a	Ph	C(CH ₃) ₂ Ph	Styrene	60	>500	2000 ^b	10,000 ^b	2	0.2	[93]
104a	Ph	C(CH ₃) ₂ Ph	Styrene	60	25,000 ^d	–	–	4.0	1.0 ^c	[214]
144a	Ph	CH ₂ Ph	Styrene	60	50	400 ^b	11,600 ^b	2	0.034	[93]
144a	Ph	CH ₂ Ph	Styrene	60–90	190	–	–	–	–	[215]
104a	Ph	C(CH ₃) ₂ Ph	Styrene	110	29	–	–	–	–	[92]
185	CH ₃	CH ₂ Ph	Styrene	110	10	–	–	–	–	[92]

^a Arrhenius parameters are provided in the reference indicated.

^b Estimated by kinetic simulation. Actual values may be higher [93].

^c E = CO₂CH₃.

^d C_{tr} corresponding to value of k_{add} shown ($C_{tr} = k_{add}/\phi/k_p$) with k_p (MA, 60 °C) 27,800 M⁻¹ s⁻¹ [216], k_p (S, 60 °C) 160 M⁻¹ s⁻¹.

^e Value of ϕ assumed in cited reference.

Table 10
Dithioesters (Z = aryl) used as RAFT agents

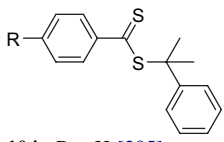
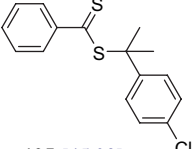
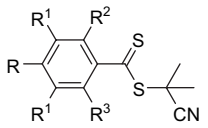
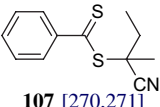
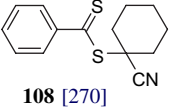
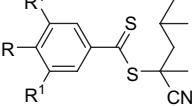
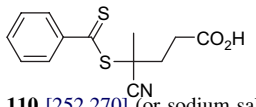
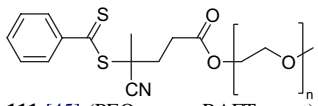
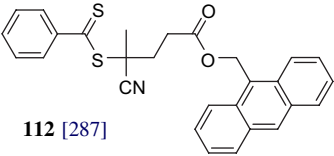
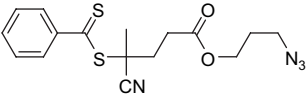
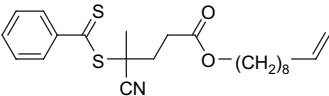
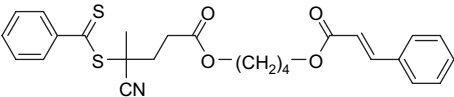
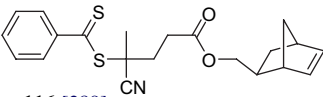
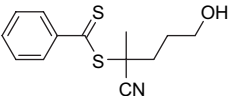
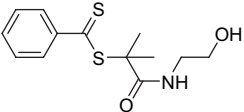
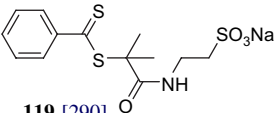
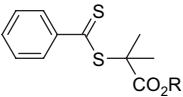
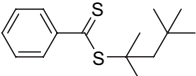
RAFT agent ^a	Polymerizations ^c
 <p>104a R = H [205]</p> <p>b R = Cl [45] c R = CH₃ [240]</p>	<p>AEMA [217] BMA [218] BMA [44,45] BzMA [91] (DBI) [219] DMAM [220] DMAEMA [221,222] GMA [222] HEMA [222,223] MMA [44,91,93,94,110,222,224–227] MMA [45] BA [228] MA [93,209,229–231] PFMA [232] NAP [233] NIPAM [233] 317 [234] 319 [235] (AN) [236] 337 [237] S [44,92,93,108,205,211,214,226,238–240] (S) [205,241–243] 325 [244] 326 [244] 2VP [245] 4VP [245] (Ip) [246] NVP [247] MMA/BA [14,248] MMA/HEMA [46] 317/MMA [234] S/HEMA [240] S/AN [44,46,222] S/MAH [222,249] S/SCI [250,251] S/NPMI [46] BzMA-<i>b</i>-DMAEMA [91] BzMA-<i>b</i>-MAA [91] MMA-<i>b</i>-MAA [91] MMA-<i>b</i>-S [91] MMA-<i>b</i>-S/AN [222] GMA-<i>b</i>-S/AN [222] HEMA-<i>b</i>-S/AN [222] DMAEMA-<i>b</i>-S/AN [222] NAP-<i>b</i>-DMAM [233] NIPAM-<i>b</i>-NAP [233] S/MAH-<i>b</i>-S/AN [222] 2VP-<i>b</i>-4VP [245] 4VP-<i>b</i>-2VP [245] MMA [45] S [240]</p>
 <p>105 [45,93]</p>	<p>MMA [45,93]</p>
 <p>106a R = R¹ = R² = R³ = H [93,205,252,253]</p> <p>b R = F, R¹ = R² = R³ = H [210] c R = CN, R¹ = R² = R³ = H [210] d R = OCH₃, R¹ = R² = R³ = H [210] e R = Ph, R¹ = R² = R³ = H [210] f R = R² = F, R¹ = R³ = H [210] g R = R² = CH₃, R¹ = R³ = H [210] h R = R² = OCH₃, R¹ = R³ = H [210] i R = R² = R³ = H, R¹ = CF₃ [210] j R = R² = R³ = H, R¹ = CN [210] k R = R¹ = R² = R³ = F [210] l R = R¹ = H, R² = R³ = CH₃ [210]</p>	<p>BMA [254] (DBI) [219] DAGMA [46,255] DMAEMA [221] EHMA [254] MMA [45,93,94,210,226,256,257] MMA [254] (NMS) [258] XMA [259,260] AA [226] BA [93] MA [93,208] 315 [261] 316 [261] 317 [234] 340 [258] 318 [262] AN [263] S [45,92,93,205,264] 343 [265] VBz [44,45] MMA/330 [266] MMA/331 [266] MA/330 [266] MA/331 [266] MA/332 [266] MA/333 [266] HPMAM/NMS [267] NIPAM/NMS [268] S/MAH [269] DAGMA-<i>b</i>-DMAEMA [255] 315-b-BMA [261] 316-b-BMA [261] 340-b-NIPAM [258] EHMA-<i>b</i>-S [254] EHMA-<i>b</i>-MMA/MA [254] 343-b-AcN [265] MMA [210,225] MMA [210] MMA [210] MMA [210] MMA [210] MMA [210] MMA [210] MMA [210] MMA [210] MMA [210] MMA [210] MMA [210]</p>
 <p>107 [270,271]</p>	<p>EEA [272] BMA [273] BzA [273] BzMA [273] DMAEMA [273] EHA [273] MA [273] MMA [273,274] <i>t</i>-BA [273]</p>
 <p>108 [270]</p>	
 <p>109a R, R¹ = H [210] b R = CN, R¹ = H [210] c R = H, R¹ = CF₃ [210] d R = OCH₃, R¹ = H [210]</p>	<p>MMA [210] MMA [210] MMA [210]</p>
 <p>110 [252,270] (or sodium salt)</p>	<p>(DBI) [219] DMAEMA [44] MMA [275] PEGMA [233] PFMA [232] 320 [276,277] 321 [276,277] 322 [276–278] AM [279] AMBA [280] AMPS [280] DMAM [233,281] DMAMPAM [281] HPMAM [282,283] MAM [284] AMPS [285] S [45,226] S [275] SSO₃Na [44,45,226,286] VBTA [281] AMPS/AMBA [285] PEGMA-<i>b</i>-344 [233] PEGMA-<i>b</i>-344-b-SCO₂H [233] AMBA-<i>b</i>-AMPS [280] AMPS-<i>b</i>-AMBA [280,285] DMAM-<i>b</i>-344 [233] DMAM-<i>b</i>-344-b-SCO₂H [233] HPMAM-<i>b</i>-DMAMPAM [283] BzMA [91] S [45,91]</p>
 <p>111 [45] (PEO macro-RAFT agent)</p>	

Table 10 (continued)

RAFT agent ^a	Polymerizations ^c
 <p>112 [287]</p>	AcN [287] AcN- <i>b</i> -MA [287]
 <p>113 [288]</p>	DMAM [288] S [288]
 <p>114 [289]</p>	MMA [289] MA [289] S [289]
 <p>115 [289]</p>	MMA [289] MA [289] S [289]
 <p>116 [289]</p>	MMA [289] MA [289] S [289]
 <p>117 [93,252,270]</p>	MMA [93,257]
 <p>118 [93]</p>	(MMA) [93]
 <p>119 [290]</p>	AM [290] TMAEMA [290]
 <p>120a R = CH₃ [550] b R = C₂H₅ [93] c R = CH₂C₆F₁₃ [293]</p>	S [549] (MMA) [93] S [93] SCI/NMPI [291] S/VBSC [292]
 <p>121 [93]</p>	(MMA) [93] S [93]

(continued on next page)

Table 10 (continued)

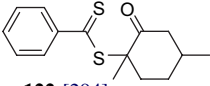
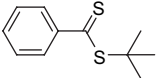
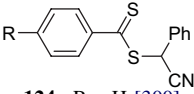
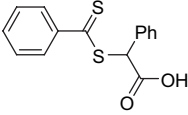
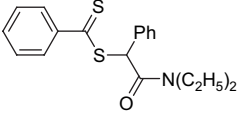
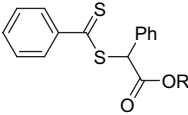
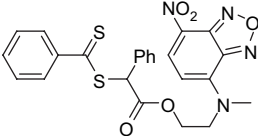
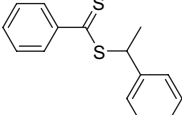
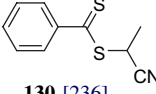
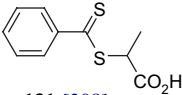
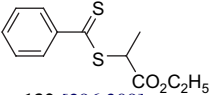
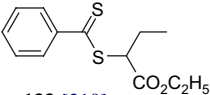
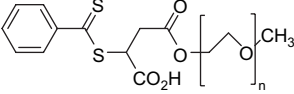
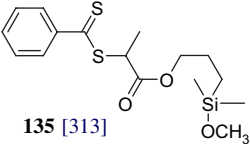
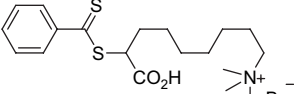
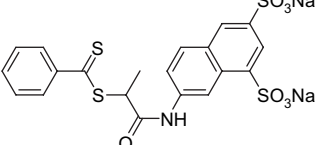
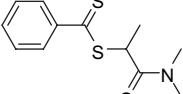
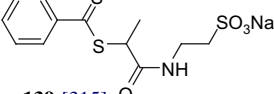
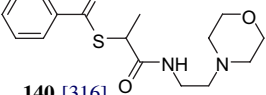
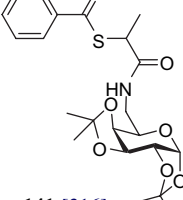
RAFT agent ^a	Polymerizations ^c
 122 [294]	NAM [294]
 123 [93,294–297]	(MMA) [93] BA [213] EHA [297] AA [298] NAM [294] ODAM [299] <i>t</i> -BAM [299] MA/VDC [296] EHA- <i>b</i> -MA [297]
 124a R = H [300] b R = OCH ₃ [300] c R = F [300] d R = Ph [300]	MMA [300] MMA- <i>b</i> -S [300] <i>t</i> -BA [300] BA [300] S [300] SAc [300] MMA [300] BA [300] S [300] BA [300] S [300] BA [300] S [300]
 125 [301]	
 126 [302,303]	DMAM [302] MA [302] S [302]
 127a R = CH ₃ [303,304] b R = PEGM [304,305] c R = PLA [304] d R = CH ₂ CH ₂ C ₆ F ₁₃ [293]	(DBI) [219] MMA [304] MA [304] DMAM [304] S [304] MMA- <i>b</i> -S [304] MMA [303–305] MMA [303,304] MMA [293] EA [293] S [293] (B) [293]
 128 [306]	BA [306]
 129 [93,295,298]	(MMA) [93] (S- <i>b</i> -MMA) [99] AA [44,45,298] MA [45,91,208,307] BA [45,91,93,205] (S) [205,242,243] BA- <i>b</i> -AA [91] MA- <i>b</i> -EA [91]
 130 [236]	AN [236]
 131 [308]	NAM [308]

Table 10 (continued)

RAFT agent ^a	Polymerizations ^c
 132 [296,309]	(MMA) [309] BA [309] S [309] MA/VDC [296]
 133 [310]	BMDO [142] S/MA [310] NPA [311] (NPA- <i>b</i> -S) [311]
 134 [312] (PEO macro-RAFT agent)	NIPAM [312]
 135 [313]	Silica- <i>g</i> -BA [313] silica- <i>g</i> -S [313]
 136 [314]	MMT- <i>g</i> -S [314]
 137 [290]	PEGA [233,290] SSO ₃ Na [233] PEGA- <i>b</i> -BA [233] SSO ₃ H- <i>b</i> - 343 [233] SSO ₃ H- <i>b</i> - 344 - <i>b</i> -SCO ₂ H [233]
 138 [220]	DMAM [220]
 139 [315]	AM [279,315]
 140 [316]	NAM [316,317]
 141 [316]	NAM [316,317]

(continued on next page)

Table 10 (continued)

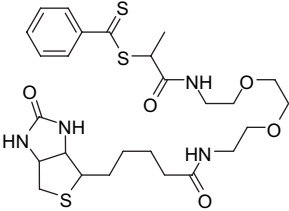
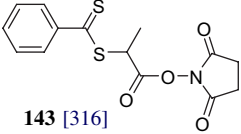
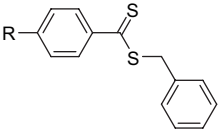
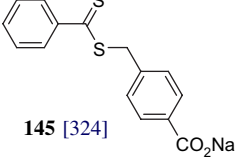
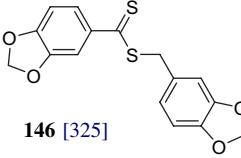
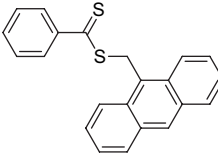
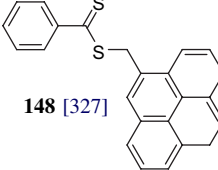
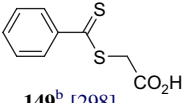
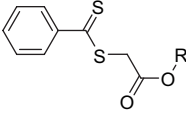
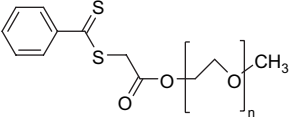
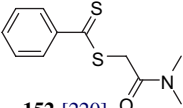
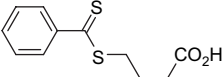
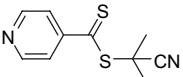
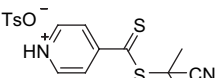
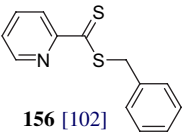
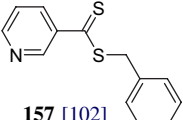
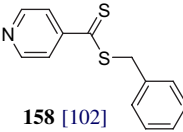
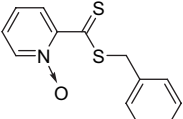
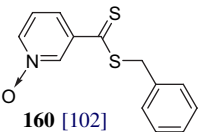
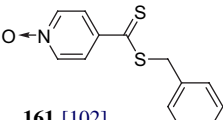
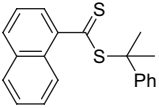
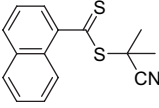
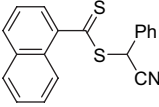
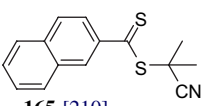
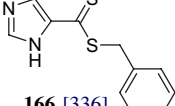
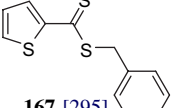
RAFT agent ^a	Polymerizations ^c
	NAM [316,317]
142 [316]	
	(Active ester precursor to other RAFT agents)
143 [316]	
	(MMA) [93] BA [93] (MA) [320] MA [93] DMAM [220] NAPM [321] S [93,215] (S) [205,242] (341) [322] 345 [323] MA/VDC [296] S- <i>b</i> -DMAM [91] S- <i>b</i> -SMe [91]
144a R = H [93,295,296,318,319]	
b R = CN [295]	(MA) [320]
c R = OCH ₃ [295]	(MA) [320]
	MMA [324]
145 [324]	
	S [325]
146 [325]	
	S [326]
147 [326]	
	S [327]
148 [327]	
	S [45] (AA) [298]
149^b [298]	
	(MMA) [309] BA [309] (S) [309] NAM [294]
150a R = CH ₃ or C ₂ H ₅ [309]	

Table 10 (continued)

RAFT agent ^a	Polymerizations ^c
b R = CH ₂ CH ₂ C ₆ F ₁₃ [293]	(MMA) [293] (S) [293] B [293]
 151 [45] (PEO macro-RAFT agent)	S [45]
 152 [220]	DMAM [220]
 153 [328]	(S) [328]
 154 [210]	MMA [210]
 155 [210]	MMA [210]
 156 [102]	S [102]
 157 [102]	S [102]
 158 [102]	S [102]
 159 [102]	(S) [102]
 160 [102]	(S) [102]
 161 [102]	(S) [102]

(continued on next page)

Table 10 (continued)

RAFT agent ^a	Polymerizations ^c
 162	MMA [329]
 163 [210,330]	MMA [210,329–331] GMA [332] S [333,334] 327 [335] MMA- <i>b</i> -S [330] 327-<i>b</i> -MMA [335] 327-<i>b</i> -S [335]
 164 [300]	MMA [300] BA [300] S [300]
 165 [210]	MMA [210]
 166 [336]	NIPAM [336]
 167 [295]	

^a References cited in this column provide a synthesis of RAFT agent.

^b RAFT agent is commercially available.

^c A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer units A then monomer units B. A-*g*-B graft of monomer B onto A. Heterogeneous polymerizations (emulsion, miniemulsion) are indicated by the monomer being in italics.

and Processes. The first output of that working party has recently been published. This is a *dilemma paper* that summarizes the current situation with respect to the polymerization kinetics, possible side reactions and mechanisms for retardation [58].

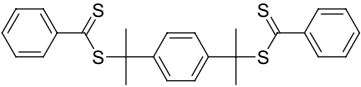
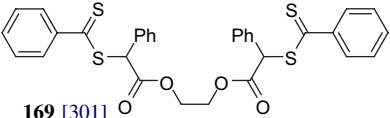
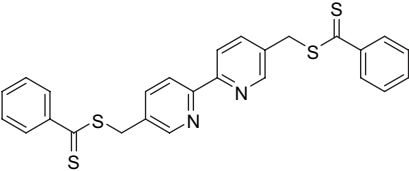
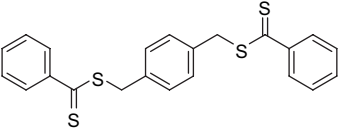
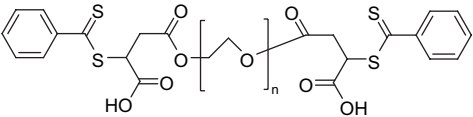
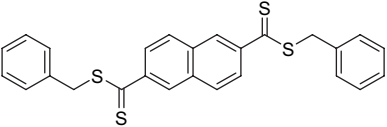
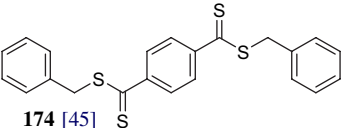
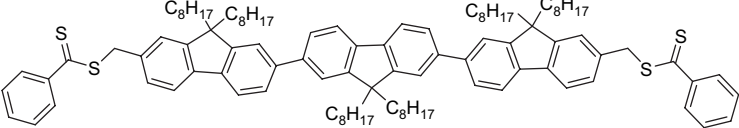
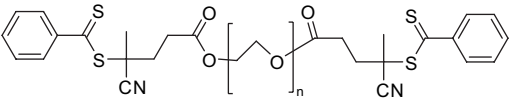
In polymerization of methacrylates and styrene with cumyl dithiobenzoate (**104a**) retardation may be observed that is directly correlated with consumption of the initial RAFT agent and which is strongly dependent on the RAFT agent concentration. Other dithiobenzoates (e.g., cyanoisopropyl dithiobenzoate (**106a**)) and aliphatic dithioesters (e.g., cumyl dithiophenylacetate) have fewer issues with respect to retardation. The aliphatic dithioesters are also less active and offer poorer control with methacrylates.

For the case of acrylates, retardation with dithiobenzoate RAFT agent is independent of 'R' and is not directly related to consumption of the initial RAFT agent, which is rapid with the dithiobenzoate being completely consumed at very low monomer conversion. Thus in polymerization of MA with benzyl (**144a**) or cyanoisopropyl dithiobenzoate (**106a**) as RAFT agent at 60 °C, substantial retardation of similar

magnitude was found from the onset of polymerization [93,94,205,206]. Use of an aliphatic dithioester and benzyl dithioacetate (**185**) provided substantially less retardation under the same polymerization conditions. Quinn et al. [207] observed that 1-phenylethyl dithiophenylacetate (**189**) enabled RAFT polymerization of MA at ambient temperature whereas 1-phenylethyl dithiobenzoate (**129**) strongly retarded polymerization under the same conditions. The observation of less retardation in RAFT polymerization of acrylate esters with aliphatic (Z = alkyl or aralkyl) and trithiocarbonate RAFT agents (Section 3.2.2) than that is seen with dithiobenzoate RAFT agents has also been reported under other circumstances [207–209]. It should be stressed that these retardation issues do not prevent formation of low polydispersity or block polymers.

Electron-withdrawing groups can enhance the activity of dithiobenzoate RAFT agents. 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 [46,210] (Fig. 3).

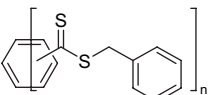
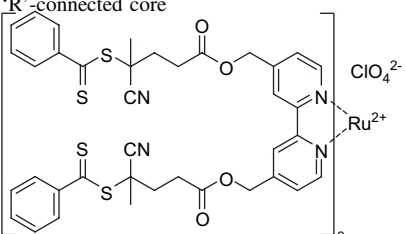
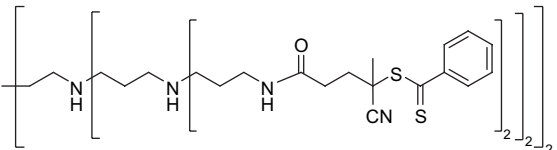
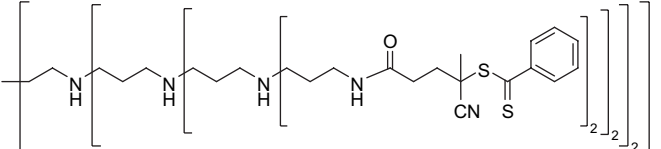
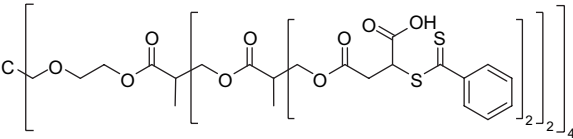
Table 11
Bis-dithioesters (Z = aryl) used as RAFT agents

RAFT agent ^a	Polymerizations ^b
'R'-connected core	
 <p>168 [45,337]</p>	BMA [91] DMAEMA [338] MMA [45,337] LMA [337] AA [338] BA [45] NAM [294] S [338] BMA- <i>b</i> -S [91] BMA- <i>b</i> -MMA [91] BMA- <i>b</i> -HEMA [91] MMA- <i>b</i> -HEMA [45] MMA- <i>b</i> -S [45]
 <p>169 [301]</p>	MMA [301] MMA- <i>b</i> -BMA [301] MMA- <i>b</i> -BA [301]
 <p>170 [339]</p>	NIPAM [339]
 <p>171 [45,337]</p>	BA [45] S [337]
 <p>172 [312] (PEO macro-RAFT agent)</p>	NIPAM [312]
'Z'-connected core	
 <p>173 [340]</p>	<i>t</i> -BA [340] S [340] S- <i>b</i> - <i>t</i> -BA [340]
 <p>174 [45]</p>	
 <p>175 [341]</p>	NIPAM [341]
 <p>176 [342] (PEO macro-RAFT agent)</p>	SSO ₃ Na [342]

^a References cited in this column provide a synthesis of RAFT agent.

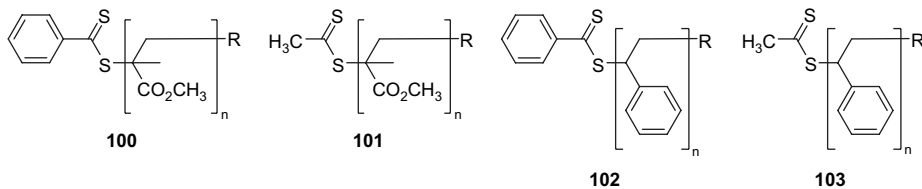
^b A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer A and monomer B. The product is a triblock. The second mentioned block is core, for 'Z'-connected examples, or the two arms, for 'R'-connected examples (Section 3.4.4).

Table 12
Multi-dithioesters (Z = aryl) used as RAFT agents

RAFT agent ^a	Polymerizations ^b
'Z'-connected core	
	<i>t</i> -BA [340] S [340]
177a <i>n</i> = 3 (1,3,5-substitution) [340]	
b <i>n</i> = 4 (1,2,4,5-substitution) [45]	S [45,91]
c <i>n</i> = 6 [45]	S [45,91,343]
'R'-connected core	
	343 [344,345] 343-<i>b</i>-AcN [345] 343-<i>b</i>-MA [346] 343-<i>b</i>-NIPAM [347]
178 [344]	
	NIPAM [349] S [348] <i>S-b</i> -MA [348]
179 [348] (8-arm dendrimer)	
	NIPAM [349] S [348] <i>S-b</i> -MA [348]
180 [348] (16-arm dendrimer)	
	NIPAM [350]
181 [350] (16-arm dendrimer)	

^a References cited in this column provide a synthesis of RAFT agent.

^b A-*b*-B block of monomer A and monomer B. The product is a triblock. The second mentioned block is core, for 'Z'-connected examples, or the two arms, for 'R'-connected examples (Section 3.4.4).

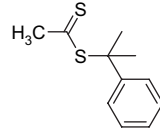
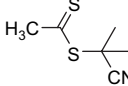
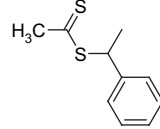
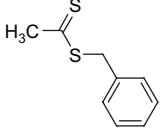
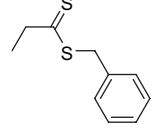
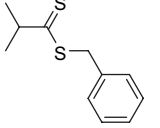
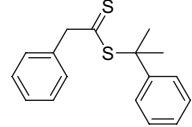
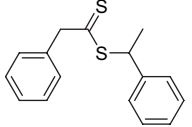
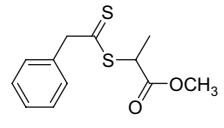
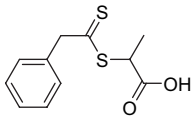
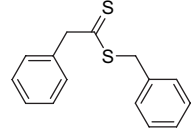


For polymeric RAFT agents used in homopolymerization where R and the propagating radical differ only in chain length and chain length is significant (>5), C_{tr}^{app} and C_{tr} ($=C_{-tr}$) are expected to be similar. In all other cases, because of the assumptions with respect to values of C_{-tr} and ϕ , C_{tr}^{app} should be regarded as a minimum value for C_{tr} . The difference between the measured C_{tr}^{app} may exceed several orders of magnitude.

3.2.2. Trithiocarbonates

The utility of trithiocarbonate RAFT agents was disclosed in the first RAFT patent [45] and many papers now describe their application (vide infra). Trithiocarbonates are less active than dithiobenzoate and similar RAFT agents (Section 3.2.1) yet still provide good control over the polymerization of (meth)acrylic and styrenic monomers. Available transfer constants data for trithiocarbonates are summarized in Table 14.

Table 13
Dithioesters (Z = alkyl or alkylaryl) used as RAFT agents

RAFT agent ^a	Polymerizations ^b	RAFT agent ^a	Polymerizations ^b
	MMA [99,226] MMA- <i>b</i> -S [99] MMA- <i>b</i> -MMA/S [99]		S [92]
182		183 [92]	
	S [99,211] (<i>S-b</i> -MMA) [99] <i>S-b</i> -MMA/S [99]		BA [44,205] S [92,242] S [45,205] <i>S-b</i> -MMA [45,205]
184		185 [92]	
	MA [320]		S/BA [351]
186 [295]		187 [351]	
	MMA [352] (NMS) [258] (DBI) [219] BA [228] MA [209,228] 336 [258] AM [279] NIPAM [353] S [241,352] NIPAM- <i>b</i> -S [353] S [354,355]		MA [207,209,356] NIPAM [353] (NVP) [357] S [243,356,358] (S [359]) S [243] S/SCI [358] NIPAM- <i>b</i> -S [353]
188 [352]		189 [207]	
	MA [212,228,360] BA [361] DA [362]		NAM [308,363] NIPAM [364] NMA- <i>b</i> -S [308]
190 [212]		191 [308]	
	MA [320] BA [233] BA- <i>b</i> -NAP [233]		
192 [233]			

^a References cited in this column provide a synthesis of RAFT agent.

^b A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer A and monomer B. Heterogeneous polymerizations (emulsion, miniemulsion) are indicated by the monomer being in italics.

More importantly, they give substantially less retardation, are less prone to hydrolytic degradation and, typically, are more readily synthesized. Ideally, to avoid odour issues with the RAFT agent and polymer the ‘Z’, and preferably the ‘R(S)’ groups, should be based on thiols with low volatility (e.g., dodecanethiol) [67,204].

A wide range of trithiocarbonate RAFT agents have now been reported, two classes are distinguished. Non-symmetrical trithiocarbonates have only one good homolytic leaving group (Table 15). The other *S*-substituent is typically primary alkyl. Symmetrical trithiocarbonates have two good homolytic leaving groups (Table 16) and the trithiocarbonate group remains in the centre of the structure as in **193** and **194**. Compounds containing two or multiple trithiocarbonate groups are listed in Tables 17 and 18.

3.2.3. Dithiocarbamates

Dithiocarbamate RAFT agents are listed in Table 19. Compounds with two dithiocarbamate groups are listed in Table 20.

N,N-Dialkyl dithiocarbamates (e.g. **256**–**268**) and *O*-alkyl xanthates (Section 3.2.4) are most suited for polymerization of VAc, NVP and related vinyl monomers where the propagating radical is a poor homolytic leaving group. The relatively low activity of simple *N,N*-dialkyl dithiocarbamate derivatives in polymerization of styrenic and (meth)acrylic monomers can be qualitatively understood in terms of the importance of the zwitterionic canonical forms (Fig. 4) which arise through interaction between the nitrogen lone pairs and the C=S double bond [92,205]. Electron-withdrawing substituents on Z can enhance the activity of RAFT agents to modify the above order [92,419,420]. Thus, dithiocarbamate RAFT agents, where the 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, can be very effective in controlling polymerization of styrenic and (meth)acrylic monomers (Table 19, e.g. **243**–**252**, **255**). Transfer constants of dithiocarbamate RAFT agents are included in Table 21.

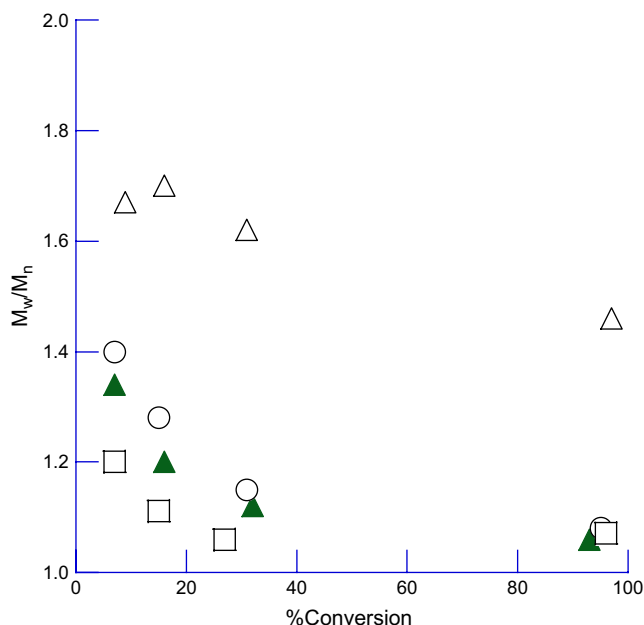


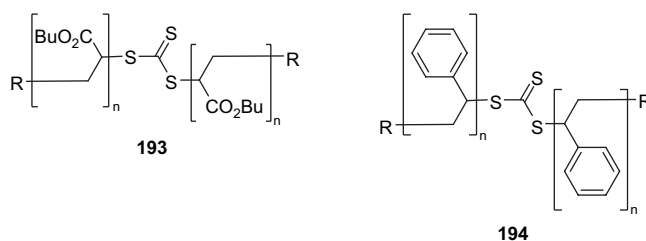
Fig. 3. Evolution of polydispersity with conversion for MMA polymerizations carried out with ring-substituted cyanoisopropyl dithiobenzoate RAFT agents: (a) 2,6-dimethyldithiobenzoate (**106l**) (Δ); (b) 4-methoxydithiobenzoate (**106d**) (\circ); (c) dithiobenzoate (**106a**) (\blacktriangle); (d) 3,5-di(trifluoromethyl)dithiobenzoate (**106i**) (\square). Figure reproduced from Ref. [46] based on data in Ref. [210].

3.2.4. Xanthates

RAFT polymerization with xanthates is sometimes called MADIX (macromolecular design by interchange of xanthate) [46,438]. Xanthate RAFT agents are listed in Table 22.

Table 14

Transfer and rate coefficients for trithiocarbonate RAFT agents



Agent	Z	R	Monomer	T (°C)	C_{tr}^{app}	k_{add} ($10^{-6} \times M^{-1} s^{-1}$)	ϕ^a	References
219	CH ₃ OCOCH(CH ₃)S	CH ₃ OCOCH(CH ₃)S	MA	60	112 ^b	2.1	0.67	[212]
219	CH ₃ OCOCH(CH ₃)S	CH ₃ OCOCH(CH ₃)S	BA	60	72 ^b	1.7	0.67	[361]
219	CH ₃ OCOCH(CH ₃)S	CH ₃ OCOCH(CH ₃)S	BA	-30	98 ^b	0.2	0.67	[101]
219	CH ₃ OCOCH(CH ₃)S	CH ₃ OCOCH(CH ₃)S	DA	60	95 ^b	2.4	0.67	[362]
193	(PBA)S	(PBA)	BA	40	220	—	—	[365]
221	PhCH ₂ S	PhCH ₂	BA	40	190	—	—	[365]
194	(PS)S	(PS)	Styrene	40	≥ 1000	—	—	[365]
207	C ₄ H ₉ S	Ph(CH ₃)CH	Styrene	110	≥ 100	—	—	[366]
224	PhthalimidomethylS	Phthalimidomethyl	Styrene	110	23	—	—	[366]
221	PhCH ₂ S	PhCH ₂	Styrene	110	18	—	—	[92]
221	PhCH ₂ S	PhCH ₂	Styrene	80	53	—	—	[365]
230	Phthalimidomethyl-CS ₂ (CH ₂) ₄ S	Phthalimidomethyl	Styrene	110	8.2	—	—	[366]
215	C ₄ H ₉ S	Phthalimidomethyl	Styrene	110	7.5	—	—	[366]

^a Value in cited paper (presumes no penultimate unit effect).

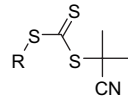
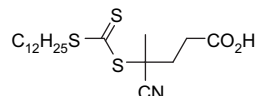
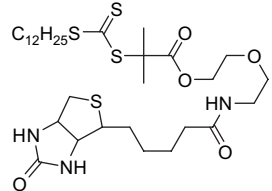
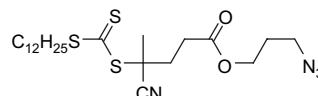
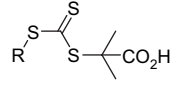
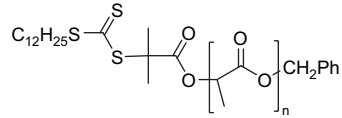
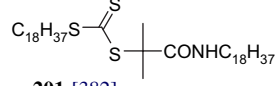
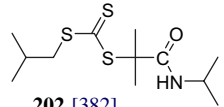
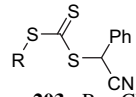
^b C_{tr} corresponding to value of k_{add} shown ($C_{tr} = k_{add}/\phi/k_p$) with k_p (MA, 60 °C) = $2.78 \times 10^4 M^{-1} s^{-1}$, k_p (BA, 60 °C) = $3.5 \times 10^4 M^{-1} s^{-1}$, k_p (BA, -30 °C) = $3.0 \times 10^3 M^{-1} s^{-1}$, k_p (DA, 60 °C) = $3.8 \times 10^4 M^{-1} s^{-1}$.

O-Alkyl xanthates have been widely exploited for RAFT polymerization of VAc, NVP and related vinyl monomers (such as NVCBz, NVI) where the propagating radical is a relatively poor homolytic leaving group. They are generally less effective (have low transfer constants) in polymerization of styrenic and acrylic monomers and offer no control for methacrylic polymers. This can be qualitatively understood in terms of the importance of the zwitterionic canonical forms (Fig. 5) [92,205]. As is the case with *N,N*-dialkyl dithiocarbamates, electron-withdrawing substituents on Z can enhance the activity of RAFT agents [92] so that they are more effective in polymerization of styrenic and (meth)acrylic monomers. Thus transfer constants of the *O*-aryl xanthates (**272–276**) are higher than those of simple *O*-alkyl xanthates. Those of fluorinated xanthates (**272**, **280**) are higher than those of non-fluorinated analogues (**275**, **286a**, respectively). Transfer constants of selected xanthate RAFT agents are included in Table 21.

O-Alkyl xanthates with appropriate selection of R have transfer constants with acrylates in the range 2–7. This is sufficient to provide end group control at high conversion (it may be possible to make block copolymers) and some trend for increase in molecular weight with conversion. It is not sufficient to provide very narrow molecular weight distributions thus most entries appear in parentheses in Table 22.

In the case of *O*-alkyl xanthates, the choice of the alkyl is crucial [439,440]. It is important that the alkyl on oxygen is a very poor homolytic leaving group with respect to the alkyl group on sulfur for cleavage of the ‘S–R’ bond to be favoured over cleavage of the ‘*O*-alkyl’ bond [440]. For example, control (predicted \bar{M}_n , low \bar{M}_w/\bar{M}_n) can be obtained in RAFT polymerization with

Table 15
Non-symmetrical trithiocarbonates (Z = thioalkyl) used as RAFT agents

RAFT agent ^a	Polymerizations ^b
 <p>195a R = CH₃ [92,252] b R = C₁₂H₂₅ [239]</p>	MMA [226,227] MA [206] S [92,226] BA/VDC [46]
 <p>196 [67]</p>	MMA [46,67]
 <p>197 [367]</p>	HPMAM [367] NIPAM [367]
 <p>198 [288]</p>	S [286] DMAM [286]
 <p>199a R = C₂H₅ [368] b R = C₁₂H₂₅ [369,370]</p>	DMAM [368]
<p>c R = CH₂CH₂CO₂H [369]</p>	323 [371] 324 [371] BA [257,369] EA [372] MA [225] AA [372,373] 334 [374] AN [373] DMAM [375] DEAM [375] EMAM [375] NIPAM [375] PAM [375] MVK [376] PVK [376] <i>t</i> -BAM [372,375] Ip [377] 334 /HEA [374] S/MAH [370,378] NIPAM/MAA [379] NIPAM/PAA [379] (NVP) [247] 334 - <i>b</i> -HEA [374] AA- <i>b</i> -EA [372] AA- <i>b</i> -S [372,380] AA- <i>b</i> -AN [373] S/MAH- <i>b</i> -Ip [378] NVP- <i>b</i> -2VP [247] MVK- <i>b</i> -S [376] PVK- <i>b</i> -S [376] BA [369]
 <p>200 [381] (PLA macro-RAFT agent)</p>	NIPAM [381] NIPAM- <i>b</i> -S [381]
 <p>201 [382]</p>	NIPAM [382,383]
 <p>202 [382]</p>	NIPAM [382]
 <p>203a R = CH₃ [47] b R = C₁₂H₂₅ [204]</p>	MMA [47] MMA [204]

(continued on next page)

Table 15 (continued)

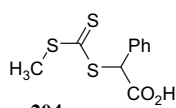
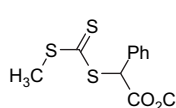
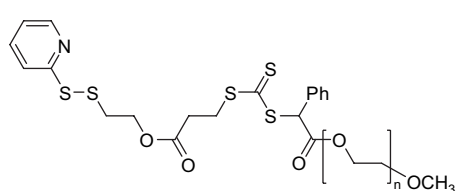
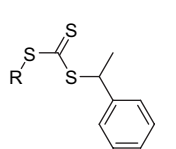
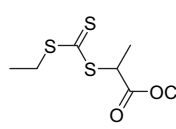
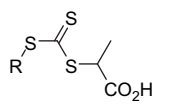
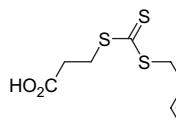
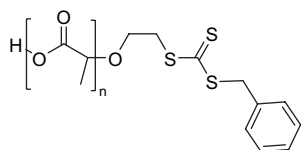
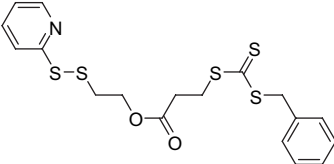
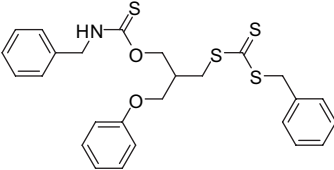
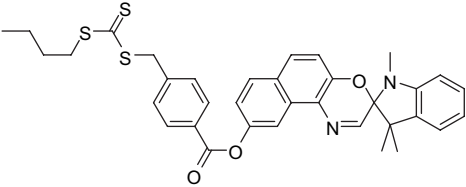
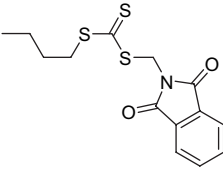
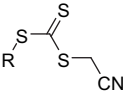
RAFT agent ^a	Polymerizations ^b
 <p>204</p>	S [226,384]
 <p>205 [303,304]</p>	(MMA) [304] MA [304] DMAM [304] S [304]
 <p>206 [385] (PEO macro-RAFT agent)</p>	(Used in synthesis of protein bound RAFT agent [385])
 <p>207a R = C₄H₉ [366] b R = C₁₂H₂₅</p>	S [366] ODA [386,387] LA/MAH [386] ODA/DMAEA [386] ODA- <i>b</i> -DMAEA [386] ODA/PEGMA [386] ODA/NVP [386,387]
<p>c R = CH₂CH₂CO₂CH₃ [240]</p>	ODA [386] ODA/DMAEA [386] ODA/GMA [386] ODA/MEP [386] ODA/MMA/MAH [386] ODA/MAA/MA [386] ODA/MA/MAH [386] ODA/MAH [386] ODA/NVP [386] ODA- <i>b</i> -DMAEA [386] ODA- <i>b</i> -MMA/MAH [386] ODA- <i>b</i> -MA/MAA [386] ODA- <i>b</i> -AA/MAH [386] ODA/DEGA [386] S [240]
 <p>208 [388]</p>	MA [388] <i>t</i> -BA [246] S [246] Ip [246] I- <i>b</i> - <i>t</i> -BA [246] I- <i>b</i> -S [246]
 <p>209a R = C₄H₉ [389] c R = CH₂CH₂CO₂H [369] b R = C₁₂H₂₅ [389]</p>	AA [389-391] AA- <i>b</i> -BA [389-391] AA- <i>b</i> -MA [389] AA- <i>b</i> -BA-S [389]
<p>c R = CH₂CH₂CO₂H [369] b R = C₁₂H₂₅ [389]</p>	BA [369] BA [257,369] MA [225] AA [389] AA- <i>b</i> -BA [389]
 <p>210 [369,392]</p>	HEMA/S [393] AA [394] BA [369,392,395] NIPAM [394] S [395] DADMAC [396,397]
 <p>211 [398] (PLA macro-RAFT agent)</p>	NIPAM [398]

Table 15 (continued)

RAFT agent ^a	Polymerizations ^b
 <p>212 [399]</p>	PEGA [399] PEGA- <i>b</i> -BA [399]
 <p>213 [400]</p>	S [400]
 <p>214 [401]</p>	BA [401] S [401] BA- <i>b</i> -S [401] S- <i>b</i> -BA [401]
 <p>215 [366]</p>	BA [386,402] NIPAM [402] (NVP) [402] S [67,366,402]
 <p>216a R = CH₃ b R = C₁₂H₂₅ [239]</p>	MA [388] BA [239] S [239]

^a References cited in this column provide a synthesis of RAFT agent.

^b A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer A and monomer B. Heterogeneous polymerizations (emulsion, mini-emulsion) are indicated by the monomer being in italics.

O-methyl, *O*-ethyl (**292**), *O*-isopropyl (**293**) and *O*-aryl xanthates but not with *O*-*tert*-butyl xanthate (**294**) [439].

It is also important to choose ‘R’ such that the radical R[•] is able to efficiently reinitiate polymerization. For example, benzyl radical is slow to add to VAc and is therefore also a poor choice for ‘R’. RAFT polymerization of VAc and NVP with *S*-phthalimidomethyl xanthate **295** gave good control over both molecular weight and polydispersity [402] (Table 23).

3.2.5. Other RAFT agents

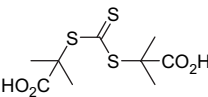
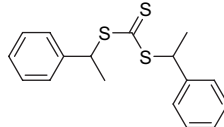
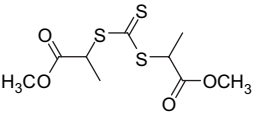
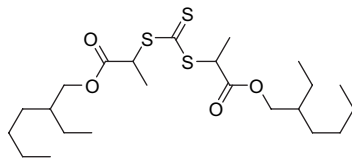
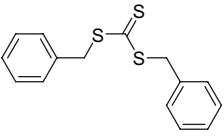
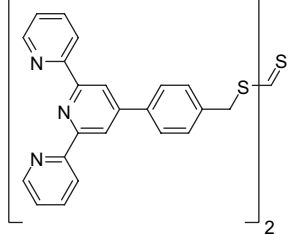
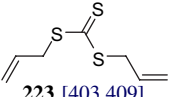
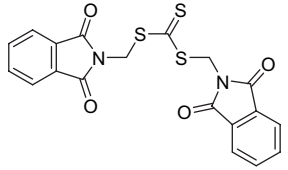
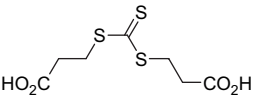
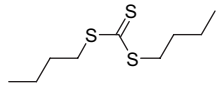
Other classes of RAFT agents are listed in (Table 24). On the basis of computational studies on RAFT agents, Z-C(=S)SR, a RAFT agent with Z = fluorine was proposed [104,107,460] as a ‘universal’ RAFT agent able to efficiently

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. The only example reported is the benzyl RAFT agent **304** and this has only been tested in styrene polymerization where limited control was observed (poor correspondence between found and calculated molecular weights, slightly narrowed polydispersity) [460].

Dithiophosphate esters (e.g., **305**) [461] have been shown to provide some control over styrene polymerization and they have been used to prepare polystyrene-*b*-PVAc. Their utility as RAFT agents has, however, been questioned on the basis of the results of computational studies [465].

Vinylogous dithioesters, in which the thiocarbonyl and the radical leaving group are separated by a conjugated unsaturated

Table 16
Symmetrical trithiocarbonates (Z = thioalkyl) used as RAFT agents

RAFT agent ^a	Polymerizations ^b	RAFT agent ^a	Polymerizations ^b
	323 [371] 324 [371] AA [372,394] BA [257,369,372] EA [372] HEA [372] MA [225] (MMA) [372] NIPAM [394] S [372] (NVP) [247] S/MAH [370] AA- <i>b</i> -EA [372] S- <i>b</i> -AA [372] EHA- <i>b</i> -EA [372]		AA [404] S [384]
	MA [212] BA [101,361,405] DA [362]		EHA [297] EHA- <i>b</i> -MA [297]
	BA [365] AA [406] AN [407] MA [388] S [92,365]		S [408] BA [408] S- <i>b</i> -BA [408] BA- <i>b</i> -S [408]
	<i>t</i> -BA [409] <i>t</i> -BA- <i>b</i> -S [409] S [409] S- <i>b</i> -BA [409]		S [366]
	(BA) [369]		(S) [366]
217 [370,372]		218 [403]	
219 [212]		220 [297]	
221 [92,388,403]		222 [408]	
223 [403,409]		224 [366]	
225 [369]		226 [366,403]	

^a References cited in this column provide a synthesis of RAFT agent.

^b A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer A and monomer B. Heterogeneous polymerizations (emulsion, mini-emulsion) are indicated by the monomer being in italics.

linkage (e.g., **308–309**), are described in the patent literature [422] but little other than passing reference has appeared in the open literature [410]. A recent paper describes the synthesis and use of **308** and **310** as RAFT agents in polymerization of EA and styrene [462]. RAFT polymerizations in the presence of **307** or **308** should provide a three-armed star.

Although for most RAFT agents the 'R' substituent is connected through carbon this is not a requirement. In RAFT agent **311** 'R' is *tert*-butylthio.

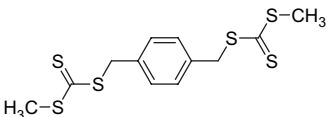
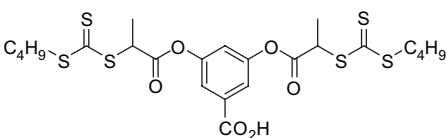
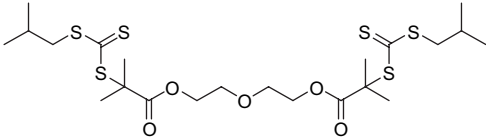
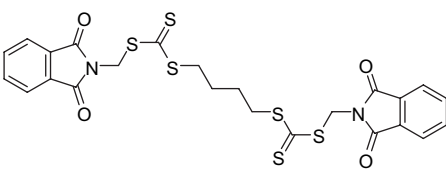
The dithioacids (e.g. **313**, **314**) are not RAFT agents since H is a poor homolytic leaving group. Dithioacids may, however, be used in RAFT polymerization when the first step is believed to be conversion of the dithioacid to a RAFT agent

which may take place by one of the several mechanisms [463]. Attempted RAFT polymerization of MA or styrene with phenyldithioacetic acid (**313**) meets with limited success [356]. However, the RAFT agent formed by Markovnikov addition of phenyldithioacetic acid to styrene (formed by pre-heating 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 [356].

3.3. Reaction conditions

Some aspects of reaction conditions to specific classes of RAFT agent have already been discussed above. This section

Table 17
Bis-trithiocarbonates used as RAFT agents

RAFT agent ^a	Polymerizations ^b
'R'-connected core	
 <p>227</p>	BA [410] BA- <i>b</i> -S/AN [410]
 <p>228 [411]</p>	BA [411] S [411]
 <p>229 [412]</p>	NIPAM [412]
'Z'-connected core	
 <p>230 [366]</p>	S [366]

^a References cited in this column provide a synthesis of RAFT agent.

^b A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer A and monomer B.

is intended to cover generic issues relating to the reaction conditions used for RAFT polymerization.

3.3.1. Temperature

Temperatures reported for RAFT polymerization range from ambient to 180 °C [238]. There is evidence with dithiobenzoates that retardation, when observed, is less at higher temperatures. Higher temperature does allow higher rates of polymerization allowing a given conversion to be achieved in a shorter reaction time. There are also some data which show that narrower molecular weight distributions can be achieved at higher temperatures [14]. This is consistent with rate constants for fragmentation of the RAFT intermediates and transfer constants of RAFT agents both increasing with reaction temperature. However, for MMA polymerization with trithiocarbonate **196** at 60 and at 90 °C (with conditions chosen to give similar rates of initiation) there appears to be no significant effect of temperature on the molecular weight or molecular weight distribution observed [46].

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 (**104a**) appears substantially less stable than benzyl or phenylethyl dithiobenzoate and degrades rapidly at temperatures >100 °C [466]. 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 **104a** was rapidly consumed and converted to more stable polymeric RAFT agents. It was also reported that the poor control observed for synthesis of PMMA with dithiobenzoate RAFT agents at higher temperatures (120 °C) could be attributed to the lability of the dithiobenzoate end group [467]. More recent work [227], 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.

RAFT polymerization of “polar” monomers (MMA, MA [468] VAc [264] and DADMAC [397]) was reported to be substantially accelerated by microwave heating. Less but still substantial acceleration was observed for styrene polymerization [264,334,468]. It is expected that monomers with a higher dielectric constant will be more effectively heated by microwave irradiation. However, the effect particularly with MMA and MA was substantially greater than expected for an effect of temperature alone [468]. An explanation for the microwave effect was not provided [468].

3.3.2. Pressure

RAFT polymerization of styrene with cumyl dithiobenzoate (**104a**) under very high pressure (5 kbar) has been reported [238,469–471]. At very 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.

3.3.3. Initiator

For optimal control of the RAFT process, it is important to pay attention to factors such as initiator concentration and selection [46]. RAFT polymerization is usually carried out with conventional radical initiators. In principle, any source of radicals can be used [45] but most often thermal initiators (e.g., AIBN, ACP, K₂S₂O₈) are used. Styrene polymerization may be initiated thermally between 100 and 120 °C. Polymerizations initiated with UV irradiation [225,472,473], a gamma source [331,394,474–480] or a plasma field [481] have also been reported. In the latter polymerizations, radicals may be generated directly from the RAFT agent and these may be responsible for initiation. It was initially suggested by Pan and coworkers that the mechanism for molecular weight control in UV [472] and gamma initiated [476,477] processes might involve only reversible coupling and be similar to that proposed by Otsu [43] to describe the chemistry of dithiocarbamate photoinitiators. However, Quinn et al. [473,478,480] demonstrated that the living behavior observed in these

Table 18
Multi-trithiocarbonates used as RAFT agents

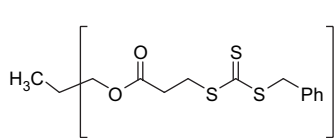
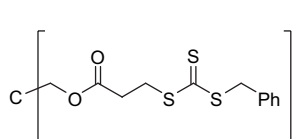
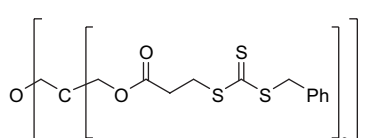
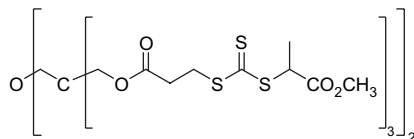
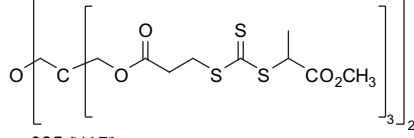
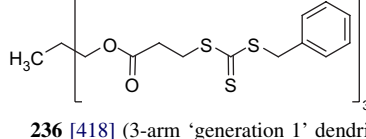
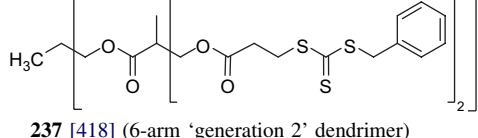
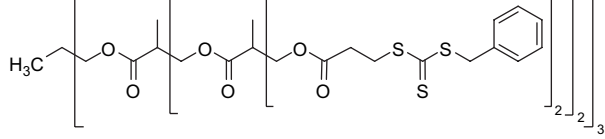
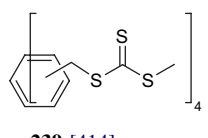
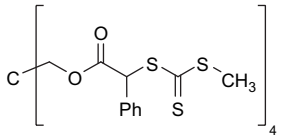
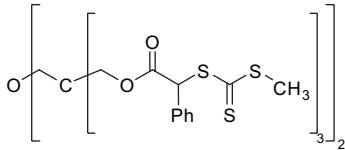
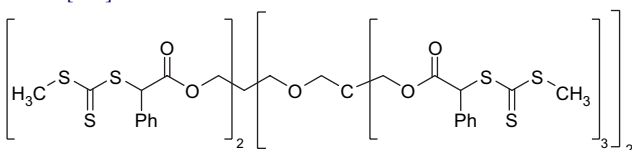
RAFT agent ^a	Polymerizations ^b
'Z'-connected core	
 <p>231 [413]</p>	
 <p>232 [413,414]</p>	<i>t</i> -BA [415] <i>t</i> -BA- <i>b</i> -S [415] MA [414] NIPAM [416] S [205,414] <i>S-b</i> -MA [414]
 <p>233 [413]</p>	
 <p>234 [417]</p>	BA [417] DA [417] MA [417]
 <p>235 [417]</p>	BA [417] MA [417] DA [417]
 <p>236 [418] (3-arm 'generation 1' dendrimer)</p>	BA [395,418] S [418] [395] <i>S-b</i> -BA [418] BA- <i>b</i> -S [418]
 <p>237 [418] (6-arm 'generation 2' dendrimer)</p>	BA [395,418] S [395,418] <i>S-b</i> -BA [418] BA- <i>b</i> -S [418]
 <p>238 [418] (12-arm 'generation 3' dendrimer)</p>	BA [395,418] S [395,418] <i>S-b</i> -BA [418] BA- <i>b</i> -S [418]
'R'-connected core	
 <p>239 [414]</p>	S [205,414] MA [414] <i>S-b</i> -MA [414]

Table 18 (continued)

RAFT agent ^a	Polymerizations ^b
	
240 [413]	
	
241 [413]	
	
242 [413]	

^a References cited in this column provide a synthesis of RAFT agent.

^b A/B – copolymerization of monomer A with monomer B. A-b-B – block of monomer A and monomer B.

polymerizations can be attributed to the standard RAFT mechanism.

The initiator concentration and rate of radical generation in RAFT polymerization should be 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 such that the target molecular weight is ~10% of that which would have been obtained in the absence of RAFT agent. A 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 excellent results (a narrow molecular weight distribution see, for example, Ref. [92]). However, 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 still lead to formation of dead chains by termination (combination or disproportionation) and consequent loss of the thiocarbonylthio end group. Addition of initiator to a RAFT-synthesized polymer is one recognized method for thiocarbonylthio end group removal [239,482].

Side reactions of the initiator or initiator-derived radicals with the RAFT agent are possible. However, these are not always readily discernable or of significance because of the high RAFT agent/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 which relates directly to the number of initiator-derived radicals. Ideally, this fraction should be taken into account when calculating the molecular weights of polymers formed by the RAFT process [92].

The molecular weight of the polymer formed can usually be estimated knowing the concentration of the monomer consumed and the initial RAFT agent concentration ($[T]$) using the relationship (7). Positive deviations from Eq. (7) indicate incomplete usage of RAFT agent. Negative deviations indicate that other sources of polymer chains are significant. These include the initiator-derived chains.

$$\bar{M}_n(\text{calc}) \sim \frac{[M]_0 - [M]_t}{[T]_0} m_M \quad (7)$$

If initiator-derived chains are significant, Eq. (8) should be used to calculate molecular weights [46].

$$\bar{M}_n(\text{calc}) \sim \frac{[M]_0 - [M]_t}{[T]_0 + df([I]_0 - [I]_t)} m_M + m_{\text{RAFT}} \quad (8)$$

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 ($d \sim 1.67$ in MMA and $d \sim 1.0$ in styrene polymerization), $[I]_0 - [I]_t$ 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 Eq. (9):

$$[I]_0 - [I]_t = [I]_0 (1 - e^{-k_d t}) \quad (9)$$

The fraction of living chains (L) in RAFT polymerization (assuming no other side reactions) is given by Eq. (10):

Table 19
Dithiocarbamates ($Z = N<$) used as RAFT agents

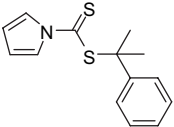
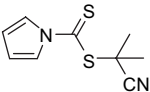
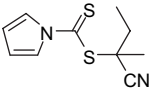
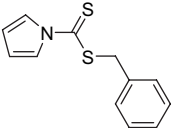
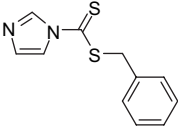
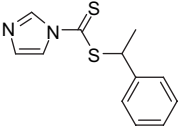
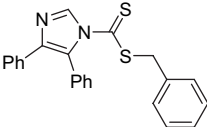
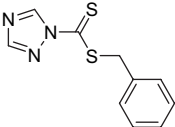
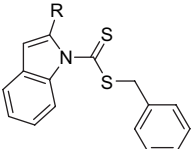
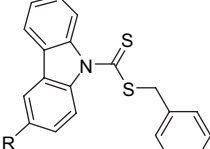
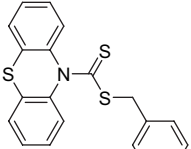
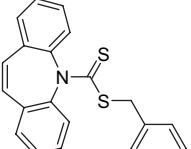
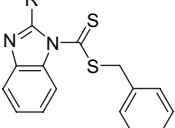
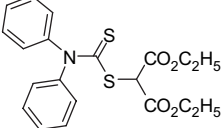
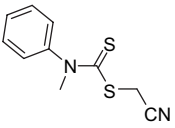
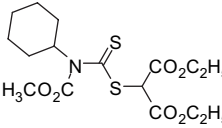
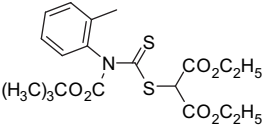
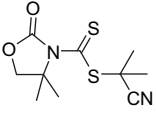
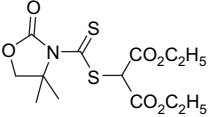
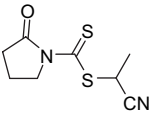
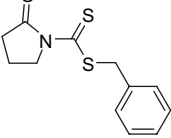
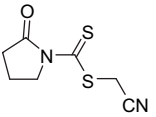
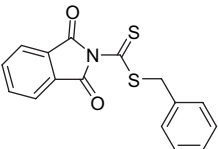
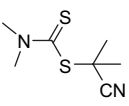
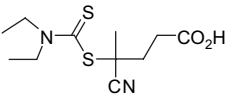
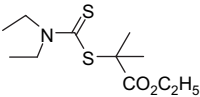
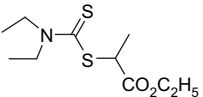
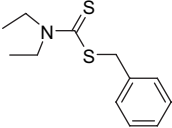
RAFT agent ^a	Polymerizations ^b	RAFT agent ^a	Polymerizations ^b
	NIPAM [258,421] (NMS) [258]		MMA [420,422] S [92]
243 [421]		244 [92,252,422]	
			MA [420] NIPAM [258,421] (NMS) [258] S [92,420] 341 [322] 342 [423]
245 [252,422]		246 [92,422]	
	S [226,420] MA [226,420] (AA) [298]		(AA) [298]
247 [422]		248 [298]	
	S [424]		S [424]
249 [424]		250 [424]	
	S [424]		S [424]
251a R = H [424] b R = Ph	S [424]	252a R = H [424] b R = PhN ₂ [425]	
	(S) [424]		(S) [424]
253 [424]		254 [424]	
	S [427]		EA [419] (VAc) [419] NVP [426]
255a R = CH ₃ [427] b R = Ph [427] c R = C ₉ H ₁₉ [428]	S [427] S [428]	256	
	VAc [46,226]		S [419] EA [419] VAc [419]
257		258	

Table 19 (continued)

RAFT agent ^a	Polymerizations ^b	RAFT agent ^a	Polymerizations ^b
 259	EA [419]	 260	(MMA) [419] S [419] VAc [419]
 261	EA [419]	 262	MA [46,206] AA [258] 340 [258] AN [46] AA- <i>b</i> -NIPAM [258,429,430]
 263 [92,422]	MA [206,226,422] (S) [92,422]	 264 [422]	
 265 [422]	(MA) [422] S [422]	 266 [252,422]	(SAc) [551]
 267 [431]	329 [431]	 268 [92,422]	VAc [226]
 268 [92,422]	(EA) [419] (VAc) [419]	 268 [92,422]	(S) [92,420]

^a References cited in this column provide a synthesis of RAFT agent.

^b A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer A and monomer B.

$$L = \frac{[7]_0}{[7]_0 + df([I]_0 - [I]_t)} \quad (10)$$

Some initiators (for example, dibenzoyl peroxide, potassium peroxydisulfate) and the derived radicals may oxidize RAFT agents to the corresponding sulfine or other products [307]. Other initiator radicals may react with the RAFT agent to form a stable thiocarbonylthio compound. It is important that the initiator-derived radical is a good leaving group with respect to the propagating radical. For example, use of an aliphatic diacyl peroxides (e.g., dilauroyl peroxide) will provide a relatively stable “RAFT agent” with R = primary alkyl. Similarly, azobis(methyl isobutyrate) (AIBMe) is not a suitable

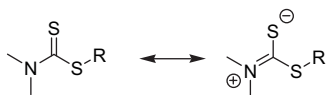


Fig. 4. Canonical forms of dithiocarbamates.

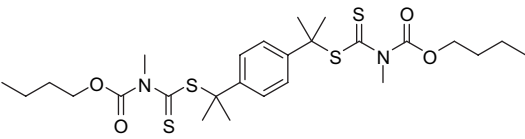
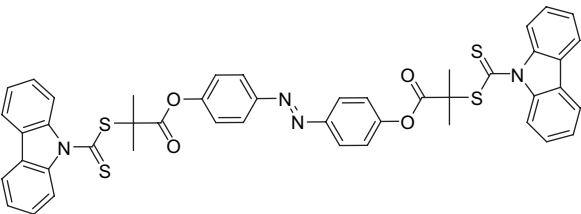
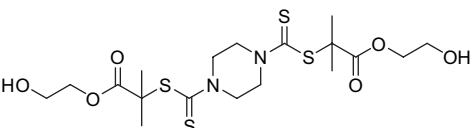
choice for RAFT polymerization of MMA. During RAFT polymerization of MMA with AIBMe and **104a** or **106a**, formation of the initiating radical-derived RAFT agent **120a** as a relatively stable byproduct is observed [94].

The mechanism of AIBN and other azonitriles decomposition are complicated by the formation of ketenimines as unstable intermediates [483]. In the presence of high concentrations of RAFT agents, the ketenimine is intercepted and converted to byproducts, which reduces the initiator efficiency and may cause some retardation.

3.3.4. Solvent

Generally, the polymerization conditions for solution or bulk RAFT polymerization are the same as those for conventional radical polymerization. The RAFT process is compatible with a wide range of reaction media including all common organic solvents, protic solvents such as alcohols and water [44,62,484] and less conventional solvents such

Table 20
Bis-dithiocarbamates (Z = N<) used as RAFT agents

RAFT agent ^a	Polymerizations ^b
'R'-connected core	
	BA [434] BA [433,435] EHA [434] <i>i</i> -OA [434] <i>t</i> -BA [434] BA/MAA [434] BA/MAA [435] BA- <i>b-i</i> -OA [435] EHA- <i>b</i> -BA [434] BA/MAA- <i>b-i</i> -OA [434]
269 [432,433]	
	S [436] S- <i>b</i> -MA [436] S- <i>b</i> -MA-NIPAM [436]
270 [436]	
'Z'-connected core	
	MMA/EA/AA [437] BA/AA/S [437] EA/S [437]
271	

^a References cited in this column provide a synthesis of RAFT agent.



^b A/B – copolymerization of monomer A with monomer B. Heterogeneous polymerizations (emulsion, miniemulsion) are indicated by the monomer being in italics. A-*b*-B block copolymers are triblocks.

as ionic liquids [485] and supercritical carbon dioxide [230,486]. It is important that RAFT agent should be selected for solubility in the reaction medium. In polar media and in the presence of Lewis acids (Section 3.3.6) RAFT agents can show hydrolytic sensitivity [276,290,487]. We have found that this order roughly correlates with RAFT agent activity (dithiobenzoates > trithiocarbonates ~ aliphatic dithioesters).

3.3.5. RAFT in heterogeneous media

Much has now been written on the use of RAFT in emulsion and miniemulsion polymerization and several reviews relating to the use of RAFT in heterogeneous media have appeared [63–66]. Our first communication on RAFT polymerization briefly mentions the successful emulsion polymerization of butyl methacrylate with cumyl dithiobenzoate as

Table 21
Transfer and rate coefficients for dithiocarbamate and xanthate (dithiocarbonate) RAFT agents

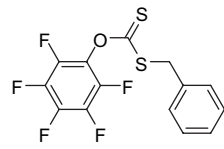
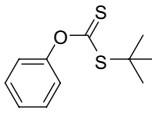
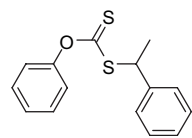
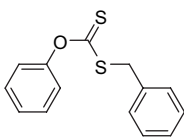
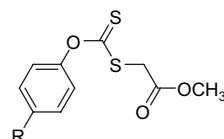
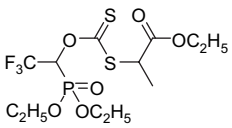
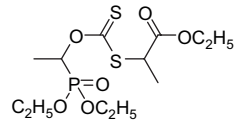
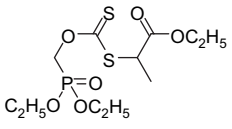
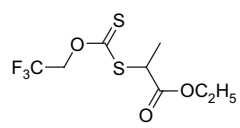
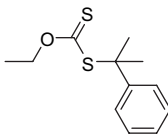
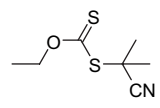
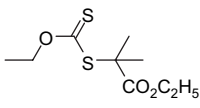
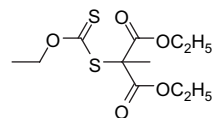
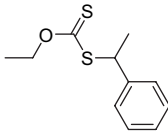
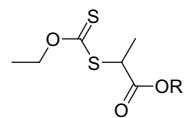
Agent	Z	R	M	<i>T</i> (°C)	C_{tr}^{app}	k_{add}^a	ϕ	References ^b
282	OC ₂ H ₅	C(CH ₃) ₂ CN	MMA	60	0.04	–	–	[422]
285	OC ₂ H ₅	CH(CH ₃)Ph	BA	60	2	–	–	[422]
282	OC ₂ H ₅	C(CH ₃) ₂ CN	<i>t</i> -BA	60	7.2	–	–	[422]
272	OC ₆ F ₅	CH ₂ Ph	<i>t</i> -BA	60	2.7	–	–	[422]
285	OC ₂ H ₅	CH(CH ₃)Ph	Styrene	60 ^b	0.65	–	–	[441]
286a	OC ₂ H ₅	CH(CH ₃)CO ₂ CH ₃	Styrene	60 ^b	0.67	–	–	[441]
280	OCH ₂ CF ₃	CH(CH ₃)CO ₂ C ₂ H ₅	Styrene	60 ^b	3.92	–	–	[441]
280	OCH ₂ CF ₃	CH(CH ₃)CO ₂ C ₂ H ₅	Styrene	60	3.8	–	–	[442]
246		CH ₂ Ph	Styrene	110	11	–	–	[92]
272	OC ₆ F ₅	CH ₂ Ph	Styrene	110	2.3	–	–	[92]
263		CH ₂ Ph	Styrene	110	1.6	–	–	[92]
275	OPh	CH ₂ Ph	Styrene	110	0.72	–	–	[92]
288	OC ₂ H ₅	CH ₂ Ph	Styrene	110	0.11	–	–	[92]
268	N(C ₂ H ₅) ₂	CH ₂ Ph	Styrene	110	0.009	–	–	[443]
286a	OC ₂ H ₅	CH(CH ₃)CO ₂ CH ₃	VAc	80	14	0.5 ^c	(0.75)	[443]

^a The unit of k_{add} is $10^6 \times M^{-1} s^{-1}$.

^b Arrhenius parameters are provided in reference indicated.

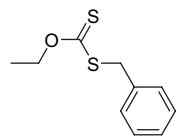
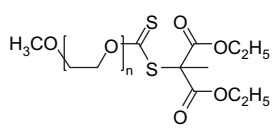
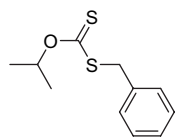
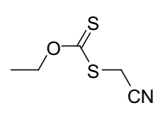
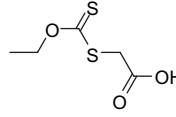
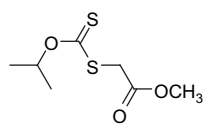
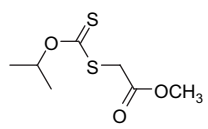
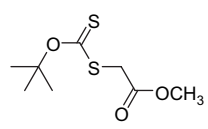
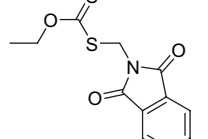
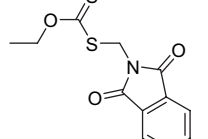
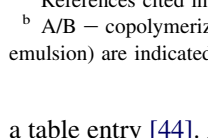
^c k_{add} estimated using k_p (VAc, 80 °C) = 47,400 $M^{-1} s^{-1}$ and with the value of ϕ shown.

Table 22
Xanthates (dithiocarbonates) (Z = alkoxy, aryloxy) used as RAFT agents^a

RAFT agent ^a	Polymerizations ^b	RAFT agent ^a	Polymerizations ^b
	(S) [92,422] MA [422] <i>t</i> -BA [422] <i>t</i> -BA/VAc [410,422] ODA [386] ODA/AN [386] ODA- <i>b</i> -NVP [386]		AA [298]
272 [92,422]		273 [298]	
	AA [298]		(S) [92,422] MA [422]
274 [298]		275 [92,422]	
	VAc [439]		EA [444] S [444]
276a R = F [439] b R = OCH ₃ [439] c R = CO ₂ CH ₃ [439] d R = CO ₂ H [439]	VAc [439] (VAc) [439] (VAc) [439]	277 [444]	
	(S) [444]		EA S [444] (S) [444]
278		279	
	EA [444] (S) [444] S [442]		(EA) [444] (AA) [298]
280		281 [298]	
	(MMA) [422] (<i>t</i> -BA) [422] (S) [444] VAc [422] VBz [422]		VAc [422]
282 [252,422]		283 [422]	
	(AA) [298]		(BA) [422] (AA) [298] NVP [357] S [422] (S) [359,446] NVCBz [447] NVI [448]
284 [298]		285 [357,422,445,446]	
	(EA) [444] MA [388] (S) [444] (S) [446] VAc [264,444] VAc [449] VNd [444] VSt [444]		
286a R = C ₂ H ₅ [388,446]			

(continued on next page)

Table 22 (continued)

RAFT agent ^a	Polymerizations ^b	RAFT agent ^a	Polymerizations ^b
b R = CH₃	AA [450] (MA/VDC) [296] AA/EAA [451] (EAA) [451] BA/EAA [451] DMAM/EAA [451] DMAEA/EAA [451] VAc [443] AA- <i>b</i> -BA [450] AA- <i>b</i> -DEGA [450]		(AA) [298] (S) [92] NVP [357]
	(AA) [298]	288 [92,298,357,445]	
287a n = 1 [298]	(AA) [298]		MA/VAc [46] VAc [422]
b n = 3 [298]	VAc [388]		
	DADMAC [396]	290 [422]	
289 [388]			AA/EAA [451] (EAA) [451] BA/EAA [451] DMAM/EAA [451] DMAEA/EAA [451] VAc [439,443]
		291 [392]	
	VAc [439]	292a R = CH₃ [439]	MA [388]
		b R = C₂H₅	(VAc) [439]
		294 [439]	
	NVP [402,452] VAc [402]		
295 [402]			

^a References cited in this column provide a synthesis of RAFT agent.

^b A/B – copolymerization of monomer A with monomer B. A-*b*-B – block of monomer A and monomer B. Heterogeneous polymerizations (emulsion, mini-emulsion) are indicated by the monomer being in italics.

a table entry [44]. Additional examples and brief discussion of some of the important factors for successful use of RAFT polymerization in emulsion and miniemulsion were provided in two patents [45,422] and in a subsequent paper [205].

It is established that success in RAFT emulsion polymerization depends strongly on the choice of RAFT agent and polymerization conditions [205,355,446,488–496]. Most work has focused on styrene polymerization [205,354,355,489,490,495,497–499], although RAFT emulsion polymerizations of BA

[389,390,491] and methacrylates [44,205] have also been reported.

The emulsion recipes we reported in our first publications [44,205] were feed processes in which conversions of monomer to polymer were maintained at a high level (often >90%). In a first *ab initio* step a low molecular weight polymeric RAFT agent was prepared which served as the seed latex and in which ideally all chains are living, i.e. capped by a thiocarbonylthio end group. Control during this stage may be relatively poor. However, the poor control obtained in this stage does not substantially affect control exerted during the later stages of polymerization as long as the ultimate molecular weight required is significantly higher than that of the initial polymeric RAFT agent. The use of cumyl dithiobenzoate (**104a**) as RAFT agent

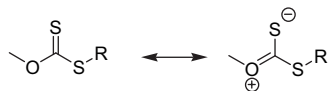
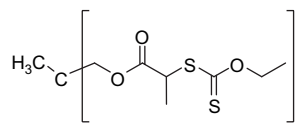
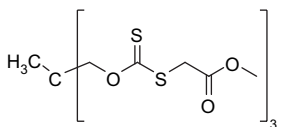
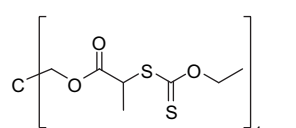
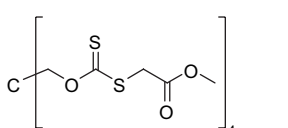
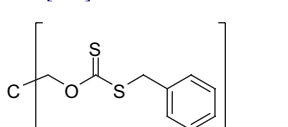
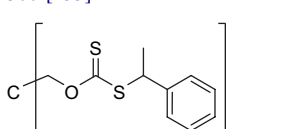


Fig. 5. Canonical forms of xanthates.

Table 23
Multi-xanthates used as RAFT agents

RAFT agent ^a	Polymerizations	RAFT agent ^a	Polymerizations
'R'-connected core		'Z'-connected core	
 <p>296 [453,454]</p>	VAc [453,454]	 <p>297 [454]</p>	VAc [454]
 <p>298 [453,454]</p>	VAc [453,454]	 <p>299 [454]</p>	VAc [454]
		 <p>300 [455]</p>	VAc [455] VPr [455]
		 <p>301 [455]</p>	VPr [455]

^a References cited in this column provide a synthesis of RAFT agent.

in *ab initio* emulsion polymerization of styrene was not recommended [205], a finding which has been borne out by many subsequent studies. However, this reagent has been successfully used for emulsion polymerization of BMA [44]. Better control in styrene emulsion polymerization is attained through the use of less active RAFT agents, such as dithioacetates, phenyldithioacetates or trithiocarbonates, than that achieved with dithiobenzoates [205,354,355]. The use of xanthate RAFT agents has also been recommended in this context [442,446].

A novel approach to RAFT emulsion polymerization has been reported which allows emulsion polymerization to be performed without added surfactant [390,493,500]. The process is analogous to the 'self-stabilizing lattices' approach we have previously used in macromonomer RAFT polymerization which involves sequential polymerization of methacrylic acid and non-polar methacrylates [501] (Section 3.1). In a first step, a water-soluble monomer (AA) was polymerized in the water phase using a water-soluble RAFT agent (**209a,b**) to form a low molecular weight macro-RAFT agent. A hydrophobic monomer (BA [389,390], styrene [497,498]) was then added under controlled feed conditions to give block oligomers which form rigid micelles. These constitute a RAFT-agent containing seed. Continued controlled feed of hydrophobic monomer may be used to continue the emulsion polymerization. A related approach to surfactant-free emulsion polymerization was reported by Freal-Saison et al. [499]. In this case the RAFT-agent containing seed was formed by bulk copolymerization of AA and

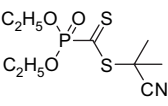
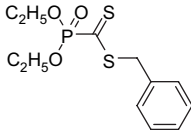
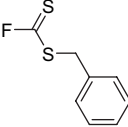
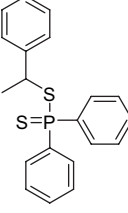
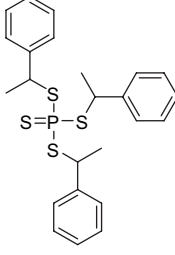
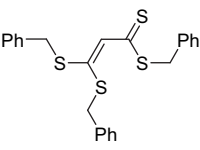
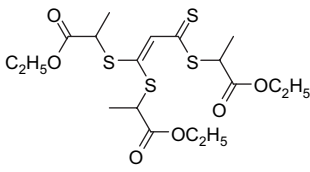
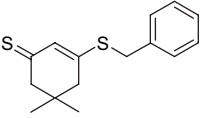
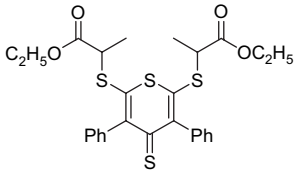
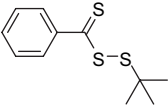
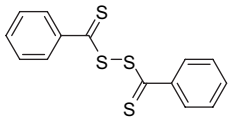
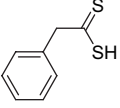
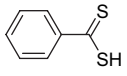
styrene with a water insoluble RAFT agent (**221**) which was neutralized before being dispersed in water. Gilbert [498] has proposed a simple theoretical model for particle formation by self-assembly during RAFT emulsion polymerization and has applied this to analyze data for styrene polymerization.

The use of RAFT to control miniemulsion polymerization has also been reported [226,243,254,391,433,449,502–511]. We showed that RAFT in miniemulsion can be used to produce narrow polydispersity polystyrene in a batch process [226]. Some retardation is observed with dithiobenzoate RAFT agents [205,243]. However, this is markedly reduced when aliphatic dithioesters [243] or trithiocarbonate RAFT agents are used [391]. One of the issues with traditional miniemulsion polymerization is the high level of surfactant and co-stabilizer that is typically employed. Pham et al. [391] have recently described surfactant-free miniemulsion polymerization. As with the emulsion procedure referred to above, amphiphatic 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 lead to a latex with no mobile surfactant and good particle size control.

3.3.6. Lewis acids

RAFT polymerization of acrylamides (NIPAM [353,512, 513], *N*-acryloyl-L-phenylalanine methyl ester [514]) and MMA [204,515,516] have been carried out in the presence of Lewis acids to obtain simultaneous control over molecular

Table 24
Other RAFT agents

RAFT agent ^a	Polymerizations	RAFT agent ^a	Polymerizations ^b
 302 [253]	MMA [253] S [253]	 303 [45,253,456]	S [45,457–459]
 304 [460]	(S) [104,460]		
 305 [461]	S [461] S- <i>b</i> -VAc [461]	 306 [461]	S [461]
 307 [422]	S [422]	 308 [462]	S [462] EA [462]
 309 [422]	S [410,422]	 310 [462]	S [462]
 311 [93]	MMA [93] BA [93]	 312 [270]	MMA [270] S [270]
 313 [552]	(MA) [356] (S) [356]	 314 [552]	MMA [463,464] MA [464] S [464]

^a References cited in this column provide a synthesis of RAFT agent.

weight and tacticity and an enhanced rate of polymerization [517]. In each case the tacticity control exerted by the Lewis acid was similar to that observed in the absence of RAFT agent. Cumyl dithiobenzoate **104a** and cyanoisopropyl

dithiobenzoate (**106a**) were found to be unstable in the presence of scandium triflate and thus unsuited for controlling MMA polymerization [204,515]. The trithiocarbonate RAFT agent (**195a**) was relatively stable and provided good control

of molecular weight, distribution and tacticity (Fig. 6) [204,515]. A recent paper describes RAFT polymerization of methyl acrylate in the presence of alumina to obtain enhanced polymerization rates [518].

Lewis acids have also been used to control the alternating tendency in RAFT copolymerization of styrene with MMA [519–521] and β -pinene with acrylonitrile [522].

3.4. Polymer architectures

3.4.1. Functional polymers

RAFT polymerization is compatible with a wide range of unprotected functionality in the monomer and RAFT agent. Examples of functional monomers are provided in Table 25 and in the tables above. Tolerated monomer functionality includes fluorine (e.g., in **315**, **316**), tertiary amino (in DMAEMA), quaternary amino (e.g., in TMAEMA), carboxylic acid (e.g., in MAA, AA, **337**, **338**), betaine (e.g., in **344**), hydroxyl (e.g., in HEA, HEMA, **317**, **320–324**, **329**), epoxy (e.g., in GMA) and thirane (in **318**) (see tables above for references). RAFT agents are generally not compatible with primary and secondary amino or with thiol functionality, though Armes and coworkers [217] have recently shown that RAFT is possible with primary amino functionality as long as it is fully protonated (in AEMA). RAFT polymerization of functional monomers has been used as a route to structures as diverse as glycopolymers (e.g., from DAGMA [46,255], **319–324**, **329** and **345**), possible hole or electron transport

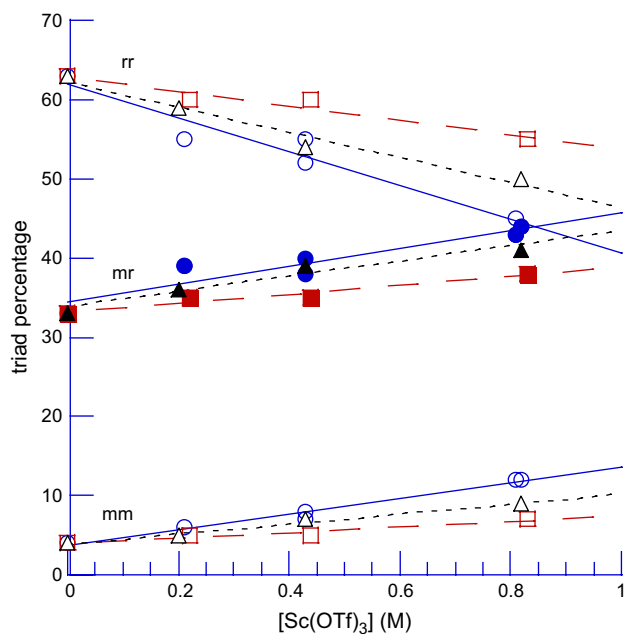


Fig. 6. Percentage of syndiotactic (*rr*), heterotactic (*mr*) and isotactic (*mm*) triads as a function of the concentration of scandium triflate during RAFT polymerization of MMA (7.01 M in benzene) at 60 °C with cyanoisopropyl methyl trithiocarbonate (**195a**) for 20–30% (— — —), 40–50% (---) and 85–95% monomer conversion (—). Figure reproduced from Ref. [515] Copyright 2007 American Chemical Society.

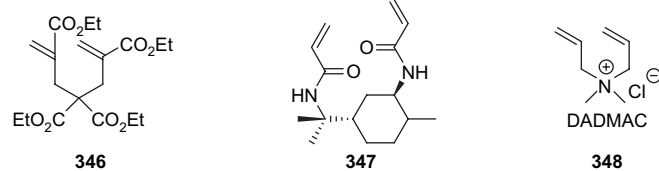
materials (e.g., from **325**, **326**, **342**), photochromic materials (e.g., from **327** [335], **330–333** [266]) and light harvesting polymers (e.g., from AcN, **343**). RAFT polymerization of activated monomers such as NAS, NMS [258,267,268] and **340** [258] also provide a means of synthesizing functional (co)polymers.

A key feature of RAFT polymerization is that the thiocarbonylthio groups, present in the initial RAFT agent, are retained in the polymeric product. This feature is responsible for the living character of RAFT polymerization and renders the process suitable for synthesizing block copolymers and end-functional polymers. However, the presence of the thiocarbonylthio groups is detrimental to some applications. Removal or transformation of the thiocarbonylthio group is therefore an integral part of many polymer syntheses.

The chemistry of the thiocarbonylthio group is well known from small molecule chemistry [85,87,88,528] and much of this knowledge has been shown applicable to transforming the thiocarbonylthio groups present in RAFT-synthesized polymers [44]. Some of the methods used for end group removal/transformation are summarized in Scheme 16. Thiocarbonylthio end groups undergo reaction with nucleophiles and ionic reducing agents such as amines [67,257,337,384, 412,414,416,487,529–533], hydroxide [421,532,534] and borohydride [62,452,532,535,536] to provide thiol end groups. This reactive end group functionality may be exploited in subsequent transformations. Thiocarbonylthio end groups also react with various oxidizing agents [44,229,307,537] (including NaOCl, H₂O₂, *t*-BuOOH, peracids, ozone) and are sensitive to UV irradiation [269,473]. Thermolysis [67,227,366,402,467, 538,539] and radical-induced reduction [67,204,239,366,526, 527,539] or termination processes [239,482] can provide complete desulfurization.

3.4.2. Cyclopolymers

The first example of RAFT cyclopolymerization (based on monomer **346**) was reported in our first RAFT patent [45]. Nagai et al. [540] have reported RAFT cyclopolymerization of the bis-acrylamide **347** with either benzyl dithiobenzoate (**144a**) or benzyl pyrrole-1-carbodithioate (**246**) as RAFT agent. Soluble products by RAFT cyclopolymerization were obtained whereas conventional radical cyclopolymerization gave some degree of crosslinking (insoluble product). It is not expected that the RAFT process should influence the efficiency of cyclization directly and this effect might simply be attributed to molecular weight control.



RAFT cyclopolymerization of DADMAC (**348**) with trithiocarbonate (**211**) or xanthate RAFT (**291**) agents has also recently been reported [396,397].

Table 25
Functional monomers used in RAFT (co)polymerization

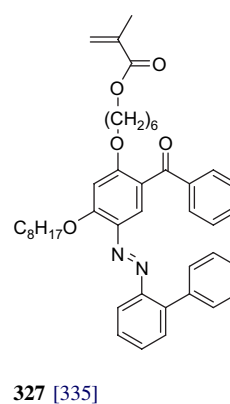
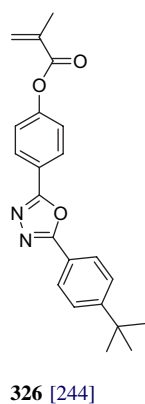
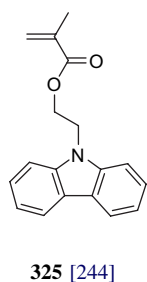
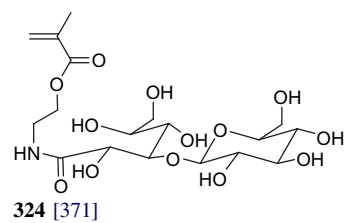
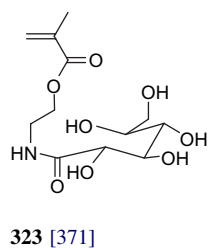
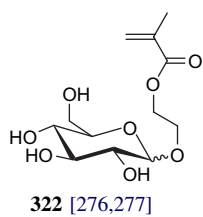
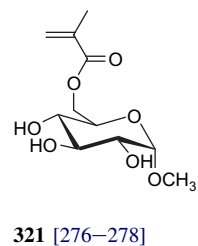
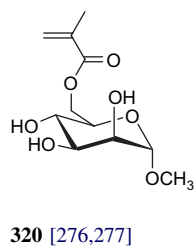
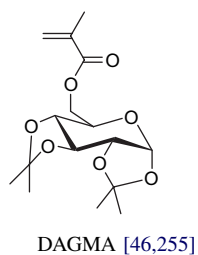
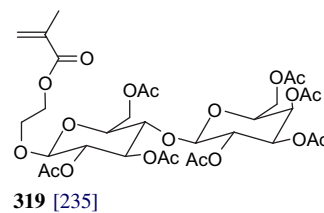
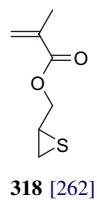
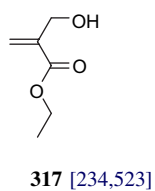
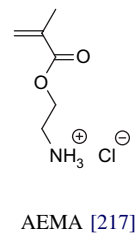
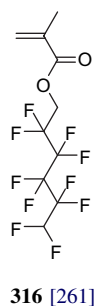
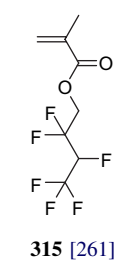
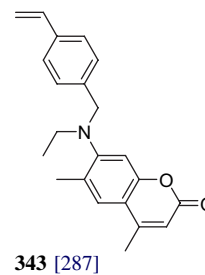
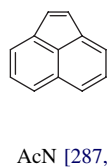
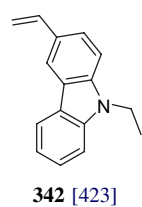
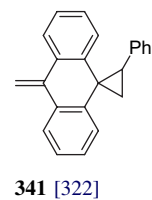
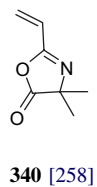
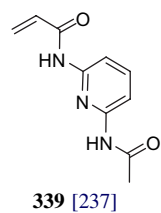
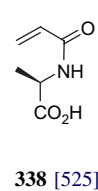
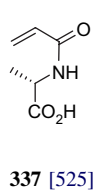
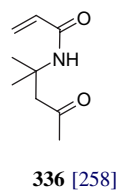
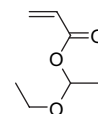
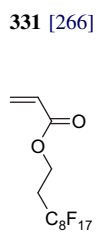
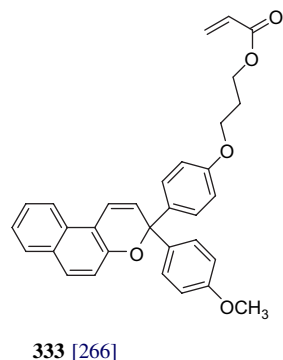
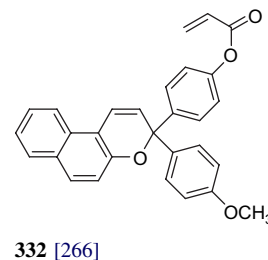
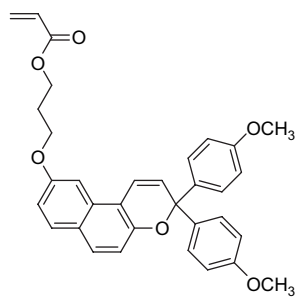
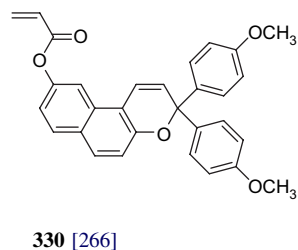
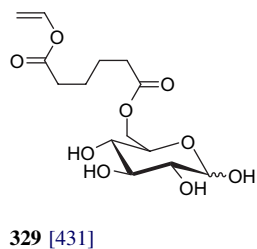
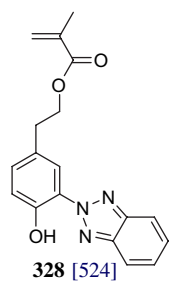
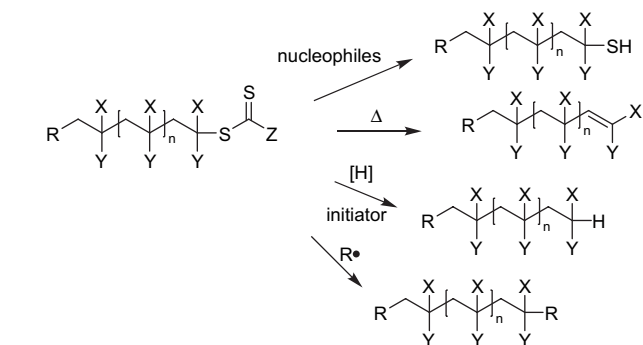


Table 25 (continued)



(continued on next page)

Table 25 (continued)



Scheme 16. Processes for end group removal ([H] = H-atom donor) [239].

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

Reactivity ratios are generally 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 differing specificity shown by the initiating species (R). The same phenomenon is observed in radical polymerization with conventional chain transfer when molecular weights are low [195,541,542]. Note that these conditions also equate to those most frequently used for measuring reactivity ratios. It is likely that the few reports of apparent dependence of reactivity ratios on the presence of RAFT agent can be attributed to this.

A wide variety of copolymers have been synthesized by RAFT polymerization and many examples are provided in the tables above (Section 3.2). 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. For example, severe retardation is observed for NVP polymerization in the presence of trithiocarbonate RAFT agents (e.g., with **215** [402]) yet copolymerization of NVP with an acrylate provides good control and little retardation (e.g., NVP/ODA with **207a** [386,387]).

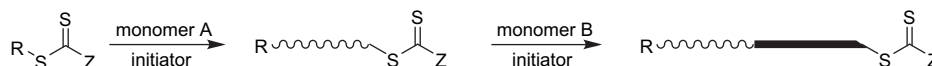
3.4.4. Block copolymers

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 thio-carbonylthio group. This allows an easy entry to the synthesis of AB diblock copolymers by the simple addition of a second monomer (Scheme 17) [91,543]. Higher order (ABA, ABC, etc.) blocks are also possible by sequential addition of further monomer(s).

Of considerable interest has been the ability to make hydrophilic–hydrophobic or double hydrophilic block copolymers where the hydrophilic block is composed of unprotected polar monomers such as AA or DMAEMA and various examples of the use of this strategy can be found in the tables above (Section 3.2).

As with other living polymerization processes, the order of constructing the blocks can be very important [91,93]. In RAFT polymerization the propagating radical for the first formed block should be chosen such that it is 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 blocks, the methacrylate block should be prepared first [91,93,99,211]. The propagating radicals sited on a styrene or acrylate unit are very poor leaving groups with respect to methacrylate propagating radicals and thus the corresponding macro-RAFT agents have extremely low transfer constants in polymerizations of methacrylate monomers.

The use of feed addition protocols, where the monomer concentration is kept low with respect to the RAFT agent



Scheme 17. AB diblock synthesis.

concentration, can be used to circumvent this requirement [205,544]. Such strategies can also allow RAFT agents with lower transfer constants ($C_{tr} \sim 0.1-5$) to be used in syntheses of polymers with narrow molecular weight distributions. Thus, while a polystyrene macro-RAFT agent appears essentially inert in batch solution polymerization of MMA, PS-*b*-PMMA has been successfully prepared by feed emulsion polymerization starting with a polystyrene macro-RAFT agent [205]. This strategy is also applied when synthesizing block copolymers from macromonomer RAFT agents (Section 3.1). Another work-around is to maintain a small amount of an appropriate comonomer in the feed [46].

For block copolymers where the leaving group ability of the propagating species is similar the order on construction is less critical. Thus, in synthesis of block copolymers of styrene with acrylic acid or with acrylate esters either block can be made first.

Block copolymers based on polymers formed by other mechanisms can be made by first preparing an end-functional pre-polymer which is converted to a polymer with thiocarbonylthio groups by end group transformation. This is then used as a macro-RAFT agent in preparation of the desired block copolymer (Scheme 18). We first exploited this methodology to prepare PEO-*b*-PS from commercially available hydroxy end-functional PEO [45,91,410]. Some further examples of this strategy to the synthesis of PEO (e.g., with macro-RAFT agents **111**, **134**, **151**, **172**, **176**, **206**) and PLA (e.g., with macro-RAFT agents **200**, **211**) block copolymers are included in the tables above.

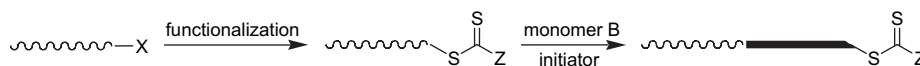
Use of a bis-RAFT agent allows the direct synthesis of triblock copolymers in a ‘one-pot’ reaction (ABA – Scheme 19, BAB – Scheme 20). Bis-RAFT agents are described in Table 11 (bis-dithioesters), Table 17 (bis-trithiocarbonates) and Table 20 (bis-dithiocarbamates). The RAFT agent functionalities may be connected through the ‘Z’ or ‘R’ groups. The

limitations of the two forms of RAFT agents are discussed below under star polymers (Section 3.4.5). Symmetrical monotrithiocarbonates (Table 16) can be considered to be in the class of ‘Z-connected’ bis-RAFT agents ($n = 0$ in Scheme 19).

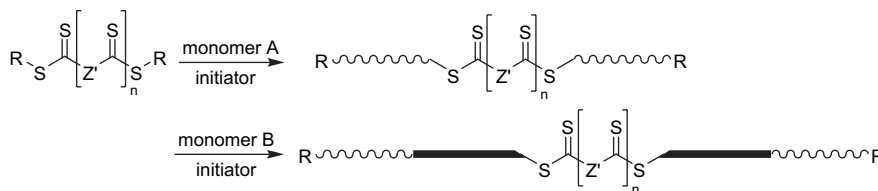
3.4.5. Star polymers

There is now a large body of literature on the synthesis of star polymers using the RAFT process [54,69,205,226,410,414,417,545,546]. A frequently used approach begins with a compound containing multiple thiocarbonylthio groups of appropriate design, a multi-RAFT agent. The multi-RAFT agent may be a small organic compound (for examples, see Tables 12, 18, and 23), an organometallic complex (e.g., **178** [344]), a dendrimer (**179**, **180** [348,349], **181** [350], **236–238** [395,418]) a hyperbranched species [392], a macromolecular species [304,547], a particle [313,314], or indeed, any moiety possessing multiple thiocarbonylthio groups (though here the distinction between star and graft copolymers may become blurred). Our first RAFT patent [45] recognized two limiting forms of star (or graft/brush copolymer) growth depending on the orientation of the thiocarbonylthio group with respect to the core. The advantages and disadvantages of the two approaches have been discussed in detail in a number of papers [414,545].

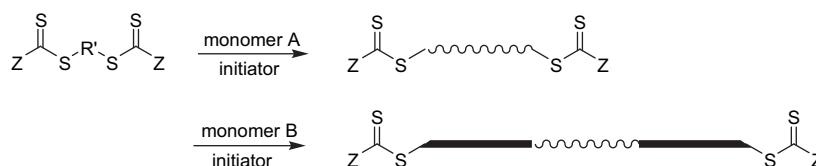
- In the first strategy the propagating radicals are linear chains that are dissociated from the core. ‘Z-connected’ RAFT agents (**349**, Scheme 21) are employed. The advantage of this strategy is that byproducts from star–star coupling are unlikely. The thiocarbonylthio functionality is retained at 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., hydrolysis, thermolysis) cause destruction of the star structure. A further potential issue is that the thiocarbonylthio



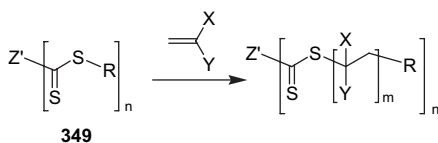
Scheme 18. A–B diblock synthesis from end-functional polymers *via* RAFT process.



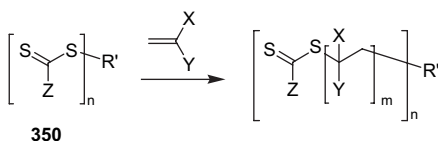
Scheme 19. A–B–A triblock synthesis from ‘Z-connected’ Bis-RAFT agent.



Scheme 20. B–A–B triblock synthesis from ‘R-connected’ Bis-RAFT agent.



Scheme 21. Star polymers' synthesis by the 'propagation away from core' strategy using a 'Z-connected' RAFT agent.



Scheme 22. Star polymers' synthesis by the 'propagation attached to core' strategy using an 'R-connected' RAFT agent.

functionality may become sterically inaccessible as polymerization proceeds.

- In the second strategy most propagating radicals remain attached to the core and 'R-connected' RAFT agents (**350**, Scheme 22) are used. Most thiocarbonylthio functionality remains on the periphery of the star. However, 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 without destroying the star structure.

Acknowledgements

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Graeme Moad obtained BSc Honours (1st Class) 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. He is also a project leader in the CRC for Polymers. Dr. Moad is author or coauthor of more than 120 papers in refereed journals, co-inventor on more than 25 patent families (including five relating to the RAFT process) and coauthor of the book “The Chemistry of Radical Polymerization” which is now in 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 CSIRO Fellow in the CSIRO Division of Molecular & Health Technologies (Melbourne). He graduated with First Class Honours in Applied Organic Chemistry from the University of NSW and was awarded a Ph.D. in Organic Chemistry by the University of Sydney in 1969 for his studies on the photochemistry of organic nitro compounds with John Pinhey. He joined David Solomon's group at CSIRO in 1976 after postdoctoral work on the synthesis of biologically active compounds with Richard Turner at Rice University (Houston), Sir Derek Barton at the Research Institute for Medicine and Chemistry (Boston), and Arthur Birch at the Australian National University (Can-

berra). At CSIRO he turned his attention to polymer science and has led research teams in the fields of Free Radical Polymerization, Polymeric Biomaterials and Engineering Polymers, and was the inaugural Director of the Cooperative Research Centre for Polymer Blends. His principal research interests are in the development of methods for understanding and controlling polymerization processes so as to produce polymers of better-defined structure and properties. Research highlights from the teams he has led include radical trapping with nitroxides, nitroxide mediated polymerization, chain transfer and ring-opening polymerization by addition–fragmentation, and the RAFT process. He is a Fellow of both the Australian Academy of Science and the Australian Academy of Technological Sciences and Engineering and the recipient of the Australian Polymer Medal, the CSIRO Chairman's Gold Medal and the Australian Government's Centenary Medal for contributions to society and polymer science.



San H. Thang arrived in Brisbane, Australia as a refugee from Vietnam in 1979. He completed his B.Sc. (Hons) in 1983 with Prof. Gus Guthrie and Ph.D. in 1987 under the supervision of Drs. Jenkins and Busfield (Griffith University) and Drs. Rizzardo and Solomon (CSIRO). San joined CSIRO in 1986 as a Research Fellow, and then moved to ICI Australia Research Group in late 1987 to undertake the challenge of industrial research in UV sunscreens and agrochemicals. He re-joined 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 has developed and held several key inventions in the area of controlled/living radical polymerization. Significantly, he is a co-inventor of the living radical polymerization by reversible addition–fragmentation chain transfer (the RAFT process).