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Review

Living Radical Polymerization by the RAFT Process – A Third Update

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This paper provides a third update to the review of reversible deactivation radical polymerization (RDRP) achieved with thiocarbonylthio compounds (ZC(=S)SR) by a mechanism of reversible addition-fragmentation chain transfer (RAFT) that was published in June 2005 (*Aust. J. Chem.* **2005**, *58*, 379). The first update was published in November 2006 (*Aust. J. Chem.* **2006**, *59*, 669) and the second in December 2009 (*Aust. J. Chem.* **2009**, *62*, 1402). This review cites over 700 publications that appeared during the period mid 2009 to early 2012 covering various aspects of RAFT polymerization which include reagent synthesis and properties, kinetics and mechanism of polymerization, novel polymer syntheses, and a diverse range of applications. This period has witnessed further significant developments, particularly in the areas of novel RAFT agents, techniques for end-group transformation, the production of micro/nanoparticles and modified surfaces, and biopolymer conjugates both for therapeutic and diagnostic applications.

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Introduction

Radical polymerization is one of the most widely used processes for the commercial production of high molar mass polymers.[1,2] The emergence of techniques for implementing reversible deactivation radical polymerization (RDRP), which serve to impart living characteristics to the process, has provided a new set of tools for polymer chemists that allow control over the polymerization process whilst retaining much of the versatility of conventional radical polymerization. It is no longer a formidable task to apply radical polymerization to the synthesis of blocks, stars, or other polymers of complex architecture. New materials with the potential of revolutionizing a large part of the polymer industry continue to appear. The polymerization techniques that are receiving greatest attention are nitroxide-mediated polymerization (NMP),[3–6] atom transfer radical polymerization (ATRP),[7–11] and reversible addition–fragmentation chain transfer (RAFT).

The controversy over the use of the terms ‘living’ and ‘controlled’ in describing processes for radical polymerizations such as ATRP, NMP, or RAFT was addressed by the International

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Ezio Rizzardo FRACI, FTSE, FAA, FRS received his Ph.D. from the University of Sydney in 1969 and joined CSIRO in 1976 after post-doctoral research at Rice University, RIMAC, and the Australian National University. His CSIRO research has focused on developing methods for controlling free radical polymerization. He is co-author of some 200 journal papers with over 14,000 citations, and co-inventor on 44 worldwide patents. He has received a number of awards including the RACI Australian Polymer Medal, the CSIRO Chairman's Gold Medal and an Australian Government Centenary Medal. In 2011, he was the co-recipient of the Prime Minister's Prize for Science.

San H. Thang completed his Ph.D. in chemistry at Griffith University in 1987. Currently, he is a chief research scientist at CSIRO Materials Science and Engineering, and an adjunct professor at Monash University. San's research focuses on the interface between biology and polymer chemistry. He has published over 100 papers which have to date received over 10,000 citations. He is responsible for several key inventions in the area of controlled/living radical polymerization; significantly, he is a co-inventor of the RAFT process. San is a Fellow of the Australian Academy of Technological Science and Engineering, and a Fellow of the Royal Australian Chemical Institute.

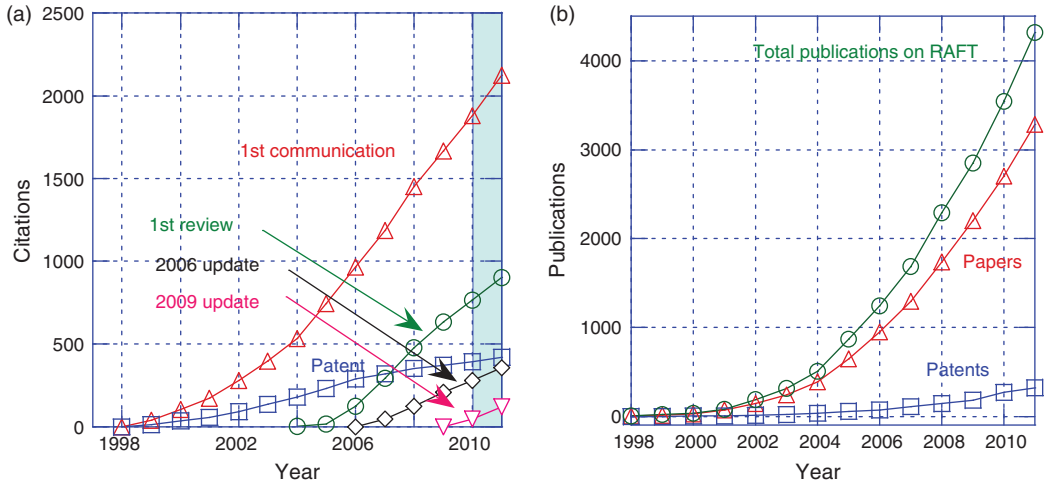


Fig. 1. (a) Cumulative citations for the authors first communication on RAFT (△),[15] first patent (□)[16] and their 2005 (○)[17] review on RAFT polymerization and its first (◇)[18] and second update (▽).[19] Based on a *SciFinder* search carried out in February 2012. (b) Total publications, papers, and patents on RAFT polymerization based on a *SciFinder* search of terms 'RAFT Polymerization', 'Reversible Addition Fragmentation Transfer' & 'radical', 'MADIX' & 'radical'. The term 'papers' includes journal articles, communications, letters, and reviews but does not include conference abstracts.

Union of Pure and Applied Chemistry (IUPAC).[12] IUPAC recommends that the term living polymerization be confined to refer to 'a chain polymerization from which irreversible chain transfer and irreversible chain termination (deactivation) are absent'. This effectively precludes use of the adjective 'living' in describing processes based on radical polymerization.[13] While it is acceptable to describe radical polymerizations such as ATRP, NMP, or RAFT as controlled polymerization, it is also regarded as inappropriate to use 'controlled' in an exclusive sense to define a particular class of polymerization processes since the word has an established, much broader, usage. Use of the terms 'controlled living', 'controlled/living', 'pseudo-living', and 'quasi-living' in this context is also discouraged. An IUPAC task group has recommended the use of a new term (controlled) reversible deactivation radical polymerization (RDRP) to describe polymerizations, such as ATRP, NMP or RAFT, which entail equilibria between active and dormant propagating species.[14] This term is not intended to have any connotations as to the fraction of living chains that might be present in a particular polymerization process and does not imply any particular degree of control.

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

The increasing importance of RAFT polymerization is illustrated by Fig. 1 which shows the cumulative citations for our first communication on RAFT with thiocarbonylthio compounds,[15] the first RAFT patent,[16] and our previous reviews in the *Australian Journal of Chemistry*.[17–19] Of course, not all papers on RAFT polymerization cite these sources, nor are all of the papers citing these documents directly relevant to RAFT polymerization. Fig. 2 shows that the remarkable growth in publication of papers covering the various forms of RDRP has continued unabated. The total number of papers that relate to

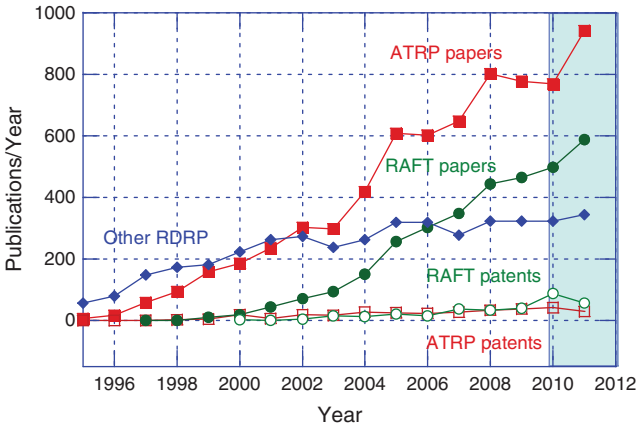
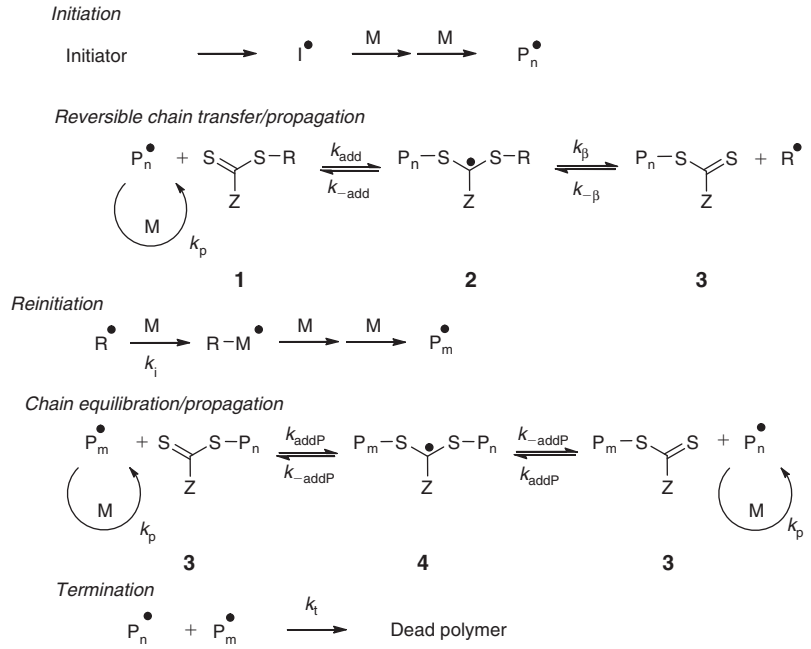


Fig. 2. Publications per year on reversible deactivation radical polymerization (RDRP) based on a *SciFinder* search in April 2012 of terms for RAFT (●) ('RAFT Polymerization', 'Reversible Addition Fragmentation Transfer', 'MADIX polymerization'), for ATRP (■) ('ATRP', 'atom transfer radical polymerization', metal-mediated radical polymerization) and for other (◆) ('nitroxide-mediated polymerization' and 'living radical polymerization', 'controlled radical polymerization' less those already counted under RAFT or ATRP). 'Papers' (closed symbols) includes journal articles, reviews, books, and letters but not conference abstracts or reports. 'Patents' (open symbols) refers to patent families.

'RAFT polymerization' has increased significantly since mid 2009 with more than 1500 papers being published and approximately one-third of papers on RDRP now pertain to the concept 'RAFT polymerization'.

This review is primarily intended to cover the literature on RAFT Polymerization that has appeared since publication of the update published in the *Australian Journal of Chemistry* in late 2009.[19] We also refer to some earlier papers that were not included in that or the earlier reviews. Work cited in the previous reviews[17–19] is only mentioned again where it is necessary to put the more recent work in context.

The last two years has seen the publication of further general reviews detailing the RAFT process, which include general reviews on RAFT polymerization.[20–25] Reviews devoted to specific areas



Scheme 1. Mechanism of RAFT polymerization.

include those on the kinetics and mechanism of RAFT polymerization,[26,27] RAFT agent design and synthesis,[28] the use of RAFT to probe the kinetics of radical polymerization,[29] microwave-assisted RAFT polymerization,[30,31] RAFT polymerization in microemulsion,[32] end-group removal/transformation,[33–36] the use of RAFT in organic synthesis,[37] the combined use of RAFT polymerization and click chemistry,[38] the synthesis of star polymers and other complex architectures,[39–42] the synergistic use of RAFT polymerization and ATRP,[43,44] the synthesis of self assembling and/or stimuli-responsive polymers,[45–47] and the use of RAFT-synthesized polymers in green chemistry,[48] polymer nanocomposites,[49–51] drug delivery and bioapplications,[41,46,47,52–60] and applications in cosmetics[61] and optoelectronics.[62] The process is also given substantial coverage in most recent reviews that, in part, relate to polymer synthesis, living or controlled polymerization or novel architectures. Some of those that include significant mention of RAFT polymerization include reviews on RDRP,[63] mechanism and reagent design,[11,64,65] click chemistry,[66–72] synthesis of telechelics,[73] the polymerization of carbazole-containing monomers,[74] *N*-vinyl-1,2,3-triazoles,[75] *N*-vinyl heterocycles,[76] fluoro-monomers,[77] and glycomonomers,[78–80] synthesis of metallopolymers,[81] conjugated block copolymers,[82] dye-functionalized polymers,[83] stimuli-responsive polymers,[84,85] complex architectures,[86,87] polyolefin blocks,[88] biopolymer–polymer conjugates and bioapplications,[59,89–93] polysaccharide modification,[94,95] polymerization in heterogeneous media,[96,97] microwave-assisted polymerization,[65,98,99] industrial prospects for RDRP,[100,101] and applications in the cosmetics industry.[102]

Mechanism of RAFT

The key feature of the mechanism of RAFT polymerization with thiocarbonylthio compounds, as proposed in our first communication on the subject,[15] is the sequence of addition–fragmentation equilibria shown in Scheme 1. Initiation and radical–radical termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical ($P_n^\bullet$) to the thiocarbonylthio compound [RSC(Z)=S (**1**)] followed by fragmentation of the intermediate radical (**2**) provides a polymeric thiocarbonylthio compound [$P_nS(Z)C{=}S$ (**3**)] and a new radical ($R^\bullet$). Reaction of this radical ($R^\bullet$) with monomer forms a new propagating radical ($P_m^\bullet$). Rapid equilibrium between the active propagating radicals ($P_n^\bullet$ and $P_m^\bullet$) and the dormant polymeric thiocarbonylthio compounds (**3**) by way of the intermediate **4** provides equal probability for all chains to grow and allows for the production of low dispersity polymers. When the polymerization is complete (or stopped), most of chains are dormant [i.e. $P_nS(Z)C{=}S$ (**3**)], which possess the thiocarbonylthio end-group, and can be isolated as stable materials.

The reactions associated with RAFT equilibria shown in Scheme 1 are in addition to those (i.e. initiation, propagation, irreversible transfer, and termination) that occur during conventional radical polymerization. In an ideal RAFT process, the RAFT agent should behave as an ideal transfer agent. Thus, as is the case with radical polymerization with conventional chain transfer, the kinetics of RAFT polymerization should not be directly affected by the presence of the RAFT agent beyond those affects attributable to the different molar mass and molar mass distribution of the reacting species. Radical–radical termination is not directly suppressed by the RAFT process. Living characteristics are imparted only when the molar mass of the polymer formed is substantially lower than that which would be formed under the same conditions but in the absence of a RAFT agent and is such that the number of polymer molecules with RAFT agent-derived ends far exceeds the number formed as a consequence of termination. Many RAFT polymerizations stray from this ideal.

The initialization process (consumption of the initial RAFT agent) in RAFT polymerization has been studied by ^{1}H NMR spectroscopy for NVP[†] with a series of xanthates which differ in

[†]For an explanation of the acronyms and abbreviations used throughout this paper please see the section entitled *Abbreviations*.

the 'R' group.[103] The selectivity of initialization (and the transfer constant of the RAFT agent) was found to depend strongly on the 'R' group. A selective initialization is one in which there is substantial conversion to a single unit adduct before any significant formation of two or higher unit adducts occurs. Xanthates **215**, **216**, **222** > **224**–**229** provided (Table 9) selective initialization and were suitable for controlling NVP polymerization with some limitations. Xanthate **221** (R = phenylethyl), which gave a long induction period, and **223** (R = *t*-butyl), which showed poor selectivity, were not recommended for use with NVP.

RAFT Transfer Constants

The efficiency of the RAFT process is determined by the values of two transfer coefficients, C_{tr} ($=k_{tr}/k_p$) and C_{-tr} ($=k_{-tr}/k_{-\beta}$). The rate coefficient for chain transfer (k_{tr}) for a RAFT agent is given by the Eqn 1. The value of k_{tr} depends on the rate of addition of the propagating radical ($P_n^\bullet$) to the RAFT agent and a partition coefficient (ϕ) which describes the partitioning of intermediate radical (**2**) between starting materials and products – refer to Scheme 1:

$$k_{tr} = k_{add}\phi = k_{add}\frac{k_\beta}{k_{-add} + k_\beta} \quad (1)$$

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

$$k_{-tr} = k_{-\beta}\phi_\beta = k_{-\beta}\frac{k_{-add}}{k_{-add} + k_\beta} \quad (2)$$

Knowledge of the partition coefficients ϕ and ϕ_β (note $\phi_\beta = 1 - \phi$) and C_{-tr} is important for an understanding of RAFT agent activity. The high reactivity of RAFT agents towards radical addition means that C_{-tr} is seldom zero. Transfer coefficients measured by methods which include an assumption that C_{-tr} is zero or that k_β is zero will typically underestimate C_{tr}. These values should be called apparent transfer coefficients C_{tr}^{app}. In some cases, values of C_{tr} may be higher than C_{tr}^{app} by *several orders of magnitude*.[104,105] A dependence of C_{tr}^{app} on the RAFT agent concentration and/or on monomer conversion is one indication that the reverse reaction is important. The spread in literature values for C_{tr}^{app} may be attributed to this effect. Note that the situation is simplified for the case of macro-RAFT agents in homopolymerization where, notwithstanding the effects of chain length, the forward and reverse reactions are the same ($C_{tr} = C_{-tr}$) and the partition coefficient ϕ should be 0.5.

For less active RAFT agents ($C_{tr} \leq 1$), transfer coefficients for RAFT agents may be determined with reasonable accuracy by the usual methods (e.g. the Mayo method). Experimental values of kinetic parameters associated with the RAFT process (addition rate constants (k_{add}), fragmentation (k_β, k_{-add}) rate constants, and forward ($C_{tr} = k_{tr}/k_p$), reverse ($C_{-tr} = k_{-tr}/k_i$) and apparent transfer coefficients (C_{tr}^{app})) that have appeared in the literature since, or which were omitted from, our previous review[19] are collected in Table 1.

Gao and Zhu[106] have provided a new analytical expression for estimating values of C_{tr} of macro-RAFT agents from knowledge of the dispersity and the monomer conversion.

RAFT Equilibrium Constants

The properties of RAFT agents are also often discussed in terms of the value of the equilibrium constants ($K = k_{add}/k_{-add}$) associated with radical addition to a thiocarbonylthio compound.[26] Rates of addition are typically high ($k_{add} \sim 10^6$–$10^8\,M^{-1}\,s^{-1}$). Thus a high equilibrium constant generally implies a low fragmentation rate for the radical adduct and an increased likelihood for retardation and/or side reaction involving this species. In a given RAFT polymerization, there are several equilibrium constants that should be considered.

- K_P ($=k_{addP}/k_{-addP}$) associated with the main equilibrium.
- K ($=k_{add}/k_{-add}$) and $K_\beta = (k_{-\beta}/k_\beta)$ associated with the pre-equilibrium.
- K_R ($=k_{addR}/k_{-addR}$) associated with the reaction of the expelled radical with the initial RAFT agent (Scheme 2). Note this is the same as K_P when $R^\bullet$ is a propagating radical.

There are other equilibrium constants to consider if penultimate group effects and the chain length dependence of the various rate constants are considered. Recent reports of values for rate constants for addition (k_{add}) and fragmentation (k_{-add}) and of the equilibrium constant K are collected in Table 2.

Theoretical calculations have been performed to rationalize the reactivity of RAFT agents and predict RAFT equilibrium and rate constants.[26,116–118] Rodríguez-Sanchez et al.[116,119] used DFT methods and frontier molecular orbital theory to predict the dependence of reactivity of RAFT agents on the 'R'[119] and 'Z' substituents.[116] However, the results are at odds both with experiment and previous theoretical calculations using *ab initio* or other methods. For example, they[116] suggest an order of reactivity decreasing in the series where Z is Ph > $PhCH_2$ > dithiocarbamate > xanthate > trithiocarbonate. DFT methods were also applied to calculate the molecular structure of dibenzyl trithiocarbonate, and predict its infrared (IR) and ultraviolet (UV-vis) spectra, dipole moment, electrical polarizability, and static first hyperpolarizability.[120]

Lin and Coote[117] indicate that *ab initio* methods should provide good (within an order of magnitude) prediction of the RAFT equilibrium constant (K_{eq}) and have used these method to estimate that between trithiocarbonate **84** and a (model) poly(MA) propagating radical. Lin and Coote[121] also found that K_{eq} was strongly chain length dependent.

Mechanisms for Retardation

Although the basic mechanism shown in Scheme 1 is generally not disputed, debate continues on the detailed kinetics of the RAFT process, the rapidity with which the various equilibria are established, and what side reactions might occur to complicate the process in specific circumstances.[26,122] In particular the mechanism(s) for retardation in RAFT polymerization mediated by, in particular, dithiobenzoate RAFT agents continue to attract significant interest. The incompatibilities of two mechanistic schemes, namely the slow fragmentation model and the intermediate radical termination model were highlighted in a 'dilemma paper' by a IUPAC task group in 2006.[126] The slow fragmentation model points to high concentrations of the intermediate radicals **2** and **4**, which are not seen by EPR. The intermediate radical termination model suggests the formation of star polymer byproducts formed by self reaction of **4** or by reaction of **4** with propagating species $P_n^\bullet$, which are not observed in the product in the predicted amounts.

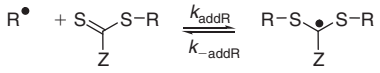
Klumpermann and Heuts[26] reexamined the previously reported calculations of Coote and co-workers and experimental determinations of rate parameters associated with RAFT polymerization using dithiobenzoate agents. They concluded that

Table 1. Transfer coefficients for RAFT agents in RAFT polymerization[A]

Agent	Z	R	Monomer	T [°C]	$C_{tr}^{app\,B}$	C_{tr}	C_{-tr}	Ref
79	$(CH_3)_2(CO_2H)CS$	$(CH_3)_2(CO_2H)C$	St	70	25.2	–	–	[107]
87	$PhC(=O)CH_2S$	$PhC(=O)CH_2$	St	70	19	–	–	[107]
91	$CH_2(CO_2H)CH_2S$	$CH_2(CO_2H)CH_2$	St	70	4.3	–	–	[107]
157	$CH_2(CO_2H)CH_2S$	$CH_3CH(CO_2H)$	St	70	13.9	–	–	[107]
126	$CH_2(CO_2H)CH_2S$	$(CH_3)_2(CO_2H)C$	St	70	20.2	–	–	[107]
175	$C_{12}H_{25}S$	$PhCH_2$	St	110	9.4	–	–	[108]
95	$C_{12}H_{25}S$	$(CH_3)_2C(CN)$	St	70	–	1875	1.6	[109]
95	$C_{12}H_{25}S$	$(CH_3)_2C(CN)$	NIPAm	70	–	1850	10	[109]
170	4-(MeO)PhS	$PhCH_2$	St	110	11.6	–	–	[108]
170	PhS	$PhCH_2$	St	110	12.4	–	–	[108]
170	4-FPhS	$PhCH_2$	St	110	18.5	–	–	[108]
170	3,4-F_2PhS	$PhCH_2$	St	110	19.5	–	–	[108]
170	4-ClPhS	$PhCH_2$	St	110	18.4	–	–	[108]
170	3,4-Cl_2PhS	$PhCH_2$	St	110	17.4	–	–	[108]
170	2,3,4,5,6-Cl_5PhS	$PhCH_2$	St	110	18.7	–	–	[108]
170	4-pyS	$PhCH_2$	St	110	22.2	–	–	[108]
170	3,5-$(CF_3)_2$PhS	$PhCH_2$	St	110	23.0	–	–	[108]
208	$PhCH(CN)C(S)S(CH_2)_4S$	PhCH(CN)	St	70	–	72	0	[110]
208	$PhCH(CN)C(S)S(CH_2)_4S$	PhCH(CN)	MMA	70	–	43	377	[110]
208	$PhCH(CN)C(S)S(CH_2)_4S$	PhCH(CN)	GMA	70	–	23	255	[110]
12	Ph	$(CH_3)_2C(CN)$	PEGMA	65	9.1	–	–	[111]
229	C_2H_5O	$C_2H_5OC(O)CH(CH_3)$	NIPAm	75	3.3	–	–	[112]
229	C_2H_5O	$C_2H_5OC(O)CH(CH_3)$	DADMAC	60	18.8	–	–	[113]
–	C_2H_5O	poly(DADMAC)	DADMAC	60	1.5	–	–	[113]
248	pyrrole	$Ph(CH_3)CH$	St	85	81	–	–	[114]
278	$(py)NCH_3$	CH_2CN	MA	70	0.9	–	–	[115]
273b	(py)N(Ph)	CH_2CN	MA	70	2.9	–	–	[115]
278-H$^+$	$(pyH^+)NCH_3$	CH_2CN	MA	70	6.9	–	–	[115]
273b-H$^+$	(py)N(Ph)	CH_2CN	MA	70	12.5	–	–	[115]
278	$(py)NCH_3$	CH_2CN	NVC	60	33.3	–	–	[115]
273b	(py)N(Ph)	CH_2CN	NVC	60	56.0	–	–	[115]
278	$(py)NCH_3$	CH_2CN	VAc	70	41.7	–	–	[115]
273b	(py)N(Ph)	CH_2CN	VAc	70	124	–	–	[115]

[A]See text for definitions of kinetic parameters and the section *Abbreviations* for the definitions of the abbreviations used here.
[B]Published values of transfer coefficients that are based on a model that does not allow for partitioning of the intermediate radicals and/or the reversibility of chain transfer are considered as apparent transfer coefficients (see text).

Reversible chain transfer



Scheme 2.

while the then available data did not allow model discrimination between the schemes, the apparent incompatibility of the models, while significant, was less than suggested in some papers. They,[26] and more recently, Junkers[27] have pointed out the need for more reliable measurements of kinetic parameters to fully resolve the situation.

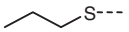
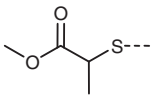
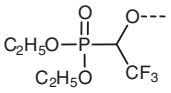
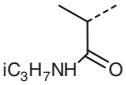
It has been pointed out that chromatography and molecular weight distributions should distinguish between the slow fragmentation and intermediate radical termination models.[127]

Two theories have been put forward to explain the absence of the star polymer by-products expected if the intermediate radical termination model applies that was mentioned in the previous update. These involve the occurrence of (a) a missing step termination or (b) short chain termination.[128] Ting et al.[129] have attempted to answer the question of whether cross-termination (between **4** and $P_n^\bullet$) might involve short radicals only. They[129] compared the rates of polymerization when a macro-azo-initiator (**5**) and a polystyrene macro-RAFT agent (**6**) were used in a RAFT polymerization of styrene (St) (this system should involve no short chain radicals) to the situation where cumyl dithiobenzoate (**11**) was the RAFT agent and azoisobutyronitrile (AIBN) was used as initiator. Other permutations were also examined. While little retardation was observed when the combination of **5** and **6** (Chart 1) was used, neither was retardation observed with **11** as RAFT agent and AIBN as initiator for higher monomer conversions (>40 %). The latter finding is inconsistent with the short chain termination model of Konkolewicz et al.[128]

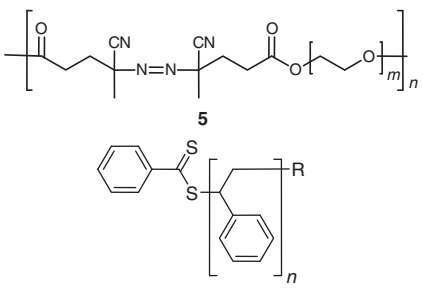
In very recent work, Meiser and Buback[130] isolated a missing-step product from the reaction of 2-cyanoprop-2-yl radicals with 2-cyanoprop-2-yl dithiobenzoate (**12**) thereby confirming the viability of this mechanism.

Chernikova et al.[118] used an EPR spin trapping method to measure addition and fragmentation rate constants for the reaction between a *t*-butyl radical and *t*-butyl dithiobenzoate (**38**). Their data analysis indicates a high value for K of $\sim 10^8\,M^{-1}$ (20°C). Meiser and Buback[123] used an EPR single pulse method to determine addition and fragmentation rate constants for the reaction between 2-cyanoprop-2-yl radicals radical and 2-cyanoprop-2-yl dithiobenzoate (**12**). Their analysis indicates a low value for K of $\sim 10^1\,M^{-1}$ (60°C). As pointed

Table 2. Values of the RAFT equilibrium constant[A]

Agent[B]	Z	R[C]	Monomer/Radical[C]	T [°C]	k_{add} [M^{-1} s^{-1}]	k_{-add} [s^{-1}]	K_{eq} [M^{-1}]	Method[D]	Ref
50	Ph---	P(BA)	BA	−40	1.4×10^6	4.7	2.3×10^5	EPR	[122]
12	Ph---			60	–	–	13	EPR	[123]
12	Ph---			100	–	–	4.6	EPR	[123]
174		P(BA)	BA	−40	–	–	1.0×10^4	EPR	[124]
84		P(MA)	MA	−30	–	–	1.4×10^4	Theory	[117]
38	Ph---			20	5×10^6	8×10^{-3}	$6(\pm 4) \times 10^8$	EPR	[118]
38	Ph---			20	–	–	4.5×10^8	Theory	[118]
219		P(BA)	BA	−40	2.5×10^4	2.3×10^3	11.1	EPR	[125]
95	$C_{12}H_{25}S$---		St	70	1×10^7	2×10^4	500	Kinetics	[109]
95	$C_{12}H_{25}S$---		NIPAm	70	1×10^7	1×10^3	1×10^4	Kinetics	[109]
95	$C_{12}H_{25}S$---			70	1×10^4	4×10^3	2.5	Kinetics	[109]
95	$C_{12}H_{25}S$---			70	1×10^4	5×10^3	2	Kinetics	[109]
95	$C_{12}H_{25}S$---			70	1×10^4	2×10^4	0.5	Kinetics	[109]

[A]See text for definition of kinetic parameters given.
[B]Initial reversible addition–fragmentation chain transfer agent used.
[C]See section entitled *Abbreviations* for definitions of acronyms and abbreviations used.
[D]EPR – determination of radical concentrations by electron paramagnetic resonsance spectroscopy; theory – *ab initio* calculations; kinetics – kinetic simulation.

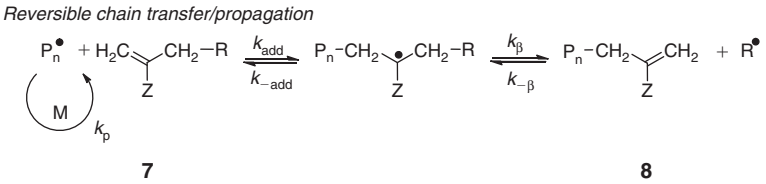


5

6 (Polystyrene macro-RAFT agent)

Chart 1.

out by Junkers et al.[131] the more than six orders of magnitude difference in K for these two systems appears surprising. It should, however, be pointed out that significantly different K values for the *t*-butyl and 2-cyanoprop-2-yl systems might be anticipated since it was already known that **12** and **38** have very different activity as RAFT agents. For example in MMA polymerization (60°C) the values of C_{tr} for **12** is ~25, and that for **38** should differ little from the value of C_{tr}^{app} 0.03;[105] a difference of 10^3. This, however, can only be attributed in part to a difference in k_{add}, it is also determined by the partition coefficient ϕ and the relative rates of fragmentation (k_{-add}) with the two RAFT agents. Chernikova et al.[118] determined k_{add} to be $\sim 10^6\,M^{-1}\,s^{-1}$. In their analysis, Meiser and



Scheme 3. Macromonomer RAFT polymerization.

Buback[123] assumed k_{add} to be $\sim 10^6\ M^{-1}\ s^{-1}$. It seems unlikely (even allowing for a temperature effect) that the k_{add} should be the same for the two radicals.

Moad et al. used ^{13}C NMR spectroscopy to follow the initiation of St polymerization with AIBN-α-^{13}C and with cumyl (**11**), 2-cyanoprop-2-yl (**15**), and benzyl dithiobenzoates (**54**) and with cyanoisopropyl dodecyl trithiocarbonate (**95**).[132] It was found that:

(1) Rates of polymerization with dithiobenzoate RAFT agents are strongly dependent on 'R' and increase in the series where R is cumyl (**11**) < 2-cyanoprop-2-yl (**15**) < benzyl (**54**).
(2) The RAFT agent does not affect the efficiency of AIBN initiation. The rate of formation of St adducts was the same for all RAFT agents.
(3) The ketenimine by-product from AIBN is converted into a stable by-product in the presence of RAFT agent. This side reaction will cause some apparent retardation since the ketenimine would normally revert to 2-cyanoprop-2-yl radicals.
(4) Some evidence for the missing step termination was observed with benzyl dithiobenzoate (**54**) as RAFT agent was observed but not with other dithiobenzoates (**11** or **15**).

Suzuki et al.[133] measured rates of dithiobenzoate-mediated St polymerization in bulk and in miniemulsion. They reported that the significantly higher rates for miniemulsion polymerization could not be simulated with the slow-fragmentation model, but could be adequately understood using the intermediate termination model assuming a relatively high fragmentation rate coefficient and a high rate coefficient for termination between the intermediate radical and a propagating radical.

Some comment should also be made on apparent rate constants for intermediate radical termination in solution. In the studies mentioned above, Chernikova et al.[118] determined k_t (intermediate radical termination) to be $6.5 \times 10^2\ M^{-1}\ s^{-1}$ (20°C). Meiser et al.[122] estimated k_t (intermediate radical termination) as 0.25 k_t (BA polymerization, 60°C).

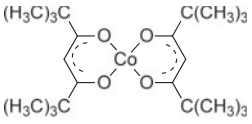
In RAFT polymerization of St with trithiocarbonate **95**, Houshyar et al.[109] found that k_t (intermediate radical termination) must be $< 10^6\ M^{-1}\ s^{-1}$ (it could be zero). Brown et al.[134] studied RAFT polymerization of St with a dithiocarbamate **254** which contains a potentially florescent carbazole chromophore to aid the detection of star products from intermediate radical termination; no stars were detected.

Further analysis is beyond the scope of this update. Suffice to say that this section does not yet have a conclusion. The mechanisms for retardation in RAFT polymerization, in systems where this is found, is not yet fully resolved.

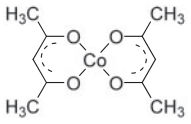
Macromonomer RAFT Polymerization

Historically, the first RAFT process used to provide living characteristics to radical polymerization was that involving so-called macromonomers (**7**, **8**, Scheme 3).[135–137] Macromonomer RAFT polymerization has been reviewed within larger reviews on catalytic chain transfer (CCT).[138,139] Similarities between the chemistry of RAFT polymerization and that seen in formation and reaction of acrylate mid chain radicals were highlighted in a recent publication.[140]

A MAA macromonomer prepared by catalytic chain transfer was used to prepare poly(MAA)-*b*-poly(BA) which was used as a reactive surfactant in emulsion polymerization of poly(MMA-*co*-BA-*co*-MAA).[141] Two papers have appeared providing a comparison of block copolymers synthesized by macromonomer RAFT polymerization with polymers of similar overall composition but synthesized by group transfer polymerization (GTP).[142,143] The copolymers synthesized by GTP had substantially better dispersity ($Đ = 1.28$) and a more homogeneous composition than those synthesized by macromonomer RAFT ($Đ = 1.7$) and their superior performance in coatings applications was considered to be a consequence of this.



9 $Co(tmhd)_2$



10 $Co(acac)_2$

Chart 2.

RAFT-Related Processes

Cobalt-Mediated Polymerization

Polymerizations of VAc and similar monomers mediated by cobalt complexes are proposed to involve a RAFT-like mechanism called associative–degenerative chain transfer (DT) or a reversible coupling mechanism, analogous to that of NMP, called organometallic radical polymerization (OMRP).[144] The relative importance of these mechanisms depend on the specific complex, the reaction conditions, and the monomers. A recent study by Kumar et al.[145] indicates that both the DT and OMRP mechanisms operate simultaneously in the case of VAc polymerization mediated by $Co(tmhd)_2$ (**9**) (Chart 2).

Control in BA polymerization or BA/VAc copolymerization was achieved with use of an alkylcobalt(III)$(acac)_2$ adduct.[146] Block copolymers of poly(VAc)-*b*-poly(VPv) or poly(VAc)-*b*-poly(VBz) were achieved by sequential monomer addition.[147] Poly(VAc) formed by cobalt-mediated polymerization with

$Co(acac)_2$ (**10**) (Chart 2) has been transformed to a polymer with a dithiobenzoate end-group to be used in RAFT polymerization of MAMs.[148]

Polymerization Mediated by Organotellurium, Organobismuthine, and Organostibine Reagents

The mechanism and application of radical polymerization mediated by organotellurium (TERP), organobismuthine, and organostibine compounds has been reviewed.[149,150] Recent papers have described the use of TERP in surfactant-free emulsion polymerization of BA[151] and St,[152,153] the preparation of polymer monoliths based on crosslinked poly(Am),[154] the use of poly(NIPAm)-*b*-poly(NVP) for solubilization of C_{60},[155] the use of heteroatom–metal exchange reactions in end-group transformation of polymers (poly(BA), poly(MMA), poly(HEMA), poly(NIPAm)) in organostibine or organobismuth-mediated polymerization[156] and the use of organostibine-mediated polymerization in St/MMA copolymerization.[157]

The end-groups of methacrylic polymers (poly(BA), poly(MMA), poly(HEMA), poly(MAN)) formed by TERP or organostibine-mediated polymerization can be eliminated to form macromonomers in high yield through reaction with (2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (and formation of an alkoxyamine intermediate) or the addition–fragmentation chain transfer agent, ethyl 2-[(tributylstannyl)methyl]acrylate.[158]

Choice of RAFT Agents

The range of thiocarbonylthio RAFT agents (ZC(=S)SR, **1**) continues to expand. The factors which influence choice of RAFT agent for a particular polymerization has been presented in various reviews.[17–19,28,137] The effectiveness of the RAFT agent depends on the monomer being polymerized and is determined by the properties of the free radical leaving group R and the group Z which can be chosen to activate or deactivate the thiocarbonyl double bond of the RAFT agent (**1**) and modify the stability of the intermediate radicals (**2**) and (**4**). For effective RAFT polymerization (Scheme 1, Fig. 3):

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

A summary of 'new' RAFT agents and polymerizations in which they and pre-existing RAFT agents have been applied is provided in Tables 3–14. These tables include some RAFT agent/monomer combinations which provide poorer molar mass control and/or $Đ > 1.4$. Generally this is indicated by the monomer appearing in parentheses. They are included because they help provide understanding of the mechanism and the construction of guidelines for the choice of RAFT agent. In some cases, poor control may reflect an inappropriate choice of RAFT agent for the monomer or unsuitable reaction conditions. In the tables, the RAFT agents generally appear in order of decreasing homolytic leaving group ability of R. Within a class (e.g. with R = tertiary cyanoalkyl), they generally appear in order of increasing complexity of R. Similarly monomers appear in order of decreasing homolytic leaving group ability of the propagating species (i.e. MAMs > LAMs and methacrylates > methacrylamides > styrenics > acrylates > acrylamides > vinyl monomers).

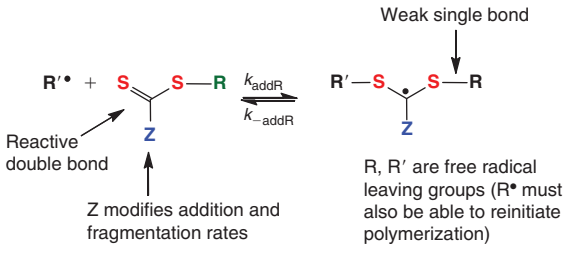


Fig. 3. Structural features of thiocarbonylthio RAFT agent and the intermediate formed on radical addition.

Several RAFT agents including dithiobenzoates, **12** and **18**, the trithiocarbonates, **89**, **95**, **98**, **123**, and **171**, and the dithiocarbamate, **258**, are now commercially available from Sigma–Aldrich[20] or Strem Chemicals.[21] Lubrizol have announced the availability of trithiocarbonate **125** in metric ton quantities.[159,160]

Dithioesters

RAFT polymerizations making use of dithioester RAFT agents are shown in Tables 3–5. Tertiary dithiobenzoates (**11**–**35**; Table 3) continue to be popular RAFT agents particularly for synthesizing polymers based on 1,1-disubsituted monomers (namely, methacrylates (e.g. MMA) or methacrylamides (e.g. HPMAm). The corresponding trithiocarbonates (**92**–**120**; Table 7) and aromatic and more active forms of the switchable dithiocarbamates (**275-H$^+$**, **276-H$^+$**; Table 13) are less active but also suitable for controlling the polymerization of these monomers. The aromatic dithioesters are more sensitive to nucleophilic attack and more prone to hydrolysis, for example, when employed in aqueous media. They are also more reactive in end-group transformation/removal reactions post RAFT polymerization.

Trithiocarbonates

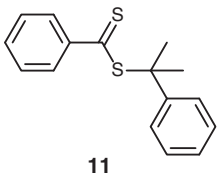
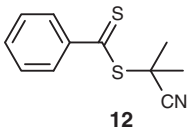
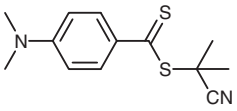
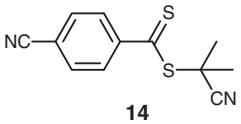
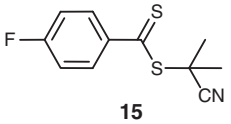
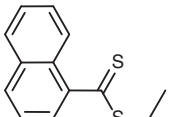
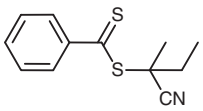
RAFT polymerizations making use of trithiocarbonate RAFT agents are shown in Tables 6–8. Two classes of trithiocarbonate RAFT agents are distinguished. Symmetrical trithiocarbonates (Table 6) that have two good homolytic leaving groups and non-symmetrical trithiocarbonates (Table 7) that have one good homolytic leaving group and a poor leaving group such as primary alkyl or aryl.[108] The Z-connected bis-trithiocarbonates shown in Table 8 also have two good homolytic leaving groups.

With symmetrical trithiocarbonates having two good homolytic leaving groups, the trithiocarbonate group usually remains in the centre of the polymer structure. However, the major product from the symmetrical trithiocarbonate **81** in MMA polymerization was the mono-macro-RAFT agent.[320] This outcome is attributed to the substantially better leaving group ability of the MMA propagating radical *v.* the monomeric analogue.

Xanthates (Dithiocarbonates)

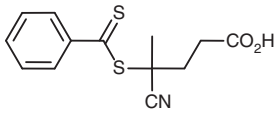
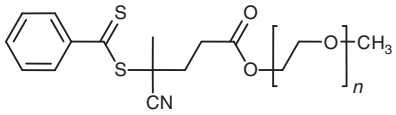
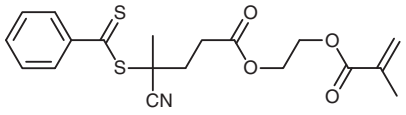
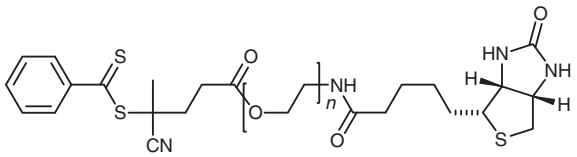
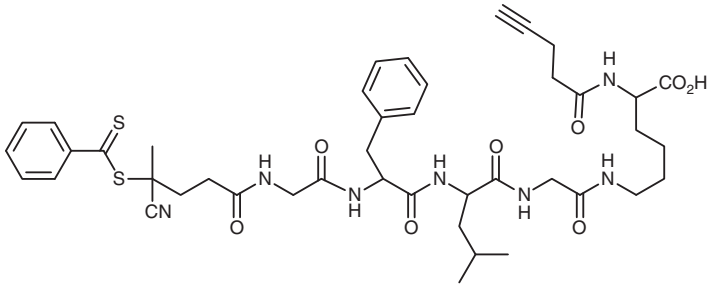
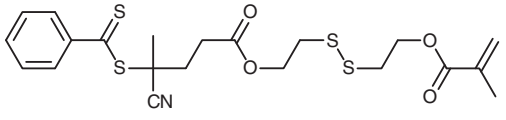
RAFT polymerization making use of xanthate (or dithiocarbonate) RAFT agents are shown in Tables 9 and 10. Xanthate RAFT agents are the most popular for controlling the polymerization of vinyl esters (e.g. VAc) and vinyl amides (e.g. NVP).

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

RAFT agent	Synthesis[A]	Polymerizations[B]
 **11**	*	BzMA[161] MMA[162] PEGMA[163] **302**[164] **301**[165] **312**[166] **396**[167] MA[168] PFPVB[169] PVS[169] St[132,162] **359**[170] St[171] BA[122] MMA/BDSMA[172] (MAA/TPMMA)[173] (MAA/**293**)[173] DEGMA/PEGMA[174] tBMA/DMAEMA/**290**[175] MMA/LMA[163] **396**-*b*-PEGMA[167] St/AcS[176] 4VP/EGDMA[177] (St-*b*-DMAEMA)[171] BzMA-*b*-HPMAm[161] DEGMA/PEGMA-*b*-DMAPMAm[174] PEGMA-*b*-MMA[163] LMA/MMA-*b*-PEGMA[163]
 **12**	D*[178]	MMA[178–184] PEGMA[111,185] GMA[186] **289**[186,187] **297**[188] **324**[189] **453**[190] iPOx[191] St[132,180,192–194] BA[122,182,194] MA[182] GA[195] iBoA[182] **342**[196] **344**[196] DEAm[193] DMAEMA/**296**[197] IPhMA/MMA[198] MMA/**314**[198] MMA/**316**[198] MAA/PEGMA[111] MMA/**329**[199] MMA/TMSMA[200] MMA/TMSMA/TMDMSOS[200] MMA/**298**[201] MMA/**299**[201] iPOx/NIPAm[191] MMA-*b*-BA/**337**[202] ***289***-*b*-*HPMA*[186,187] **342**-*b*-**344**[196] **344**-*b*-**342**[196] MMA/TMSMA-*b*-PFS[200] MMA/TMSMA/TMDMSOS-*b*-PFS[200] **324**-*b*-**292**[189] St-*b*-St/**415**[192]
 **13**	–	MMA[180] St[180] MMA-*b*-St[180] St-*b*-4MS[180]
 **14**	*	**290**/**417**[203]
 **15**	*	**322**[204] **322**/GMA[204]
 **16**	*	MMA[205,206] St[171] (St-*b*-DMAEMA)[171]
 **17**	*	MAA[207] DEGMA[208] **303**[209] **294**[210] MAA-b-AA[207] MAA/AA[207] DEGMA-*b*-DMAEMA[208] **291**/PEGMA[211] **305**/MMA[212]

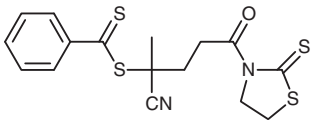
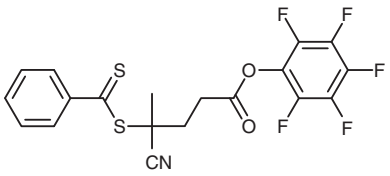
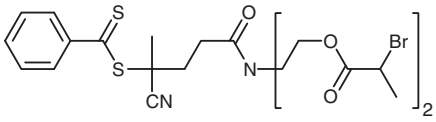
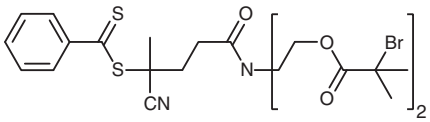
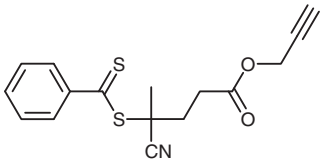
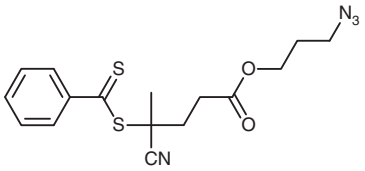
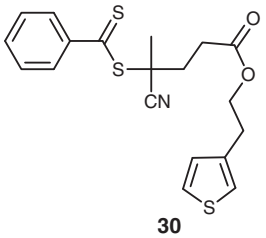
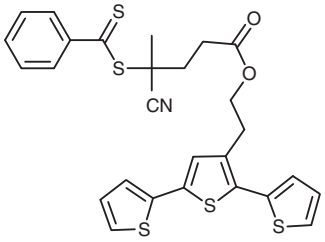
(*Continued*)

Table 3. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **18**	D*[213,214]	MAA[215] DEAEMA[216] DMAEMA[217] AEMA[218,219] MMA[220] DMAEA[221] MPC[222] PEGMA[223,224] PFPMA[225–228] **289**[229] **313**[216,230] **318**[166] **319**[231] **318**[232] **323**[233] **327**[234] **407**[235] AEMAm[236] APMAm[218,236] HPMAm[220,237,238] **355**[239] St[169,234] (PFPVS)[169] HA[240] MA[241] PFPA[228] **338**[242] (**412**)[243] Am[244] AMPS[245,246] NIPAm[241,247] (NVP)[248] MAA/PEGMA[111] MAA/**325**[249] PFPMA/LMA[225] PFPMA/PFPA[228] MPC/**320**[222] MPC/**352**[222] MPC/**353**[222] **327**-*b*-DEAm[234] ***289***-*b*-*HPMA*[229] AMPS-*b*-**363**[245,246] AEMAm/**354**[236] APMAm/**354**[236] HPMAm/**410**[250] AEMA-*b*-HPMAm[218,219] HPMAm/APMAm[251] **313**-*b*-HEMA-*b*NIPAm[230] DEAEMA-*b*-**313**[216] DMAEMA-*b*-HEMA[217] DMAEMA/PEGMA[223] PEGMA-b-DMAEMA[223] PFPMA-*b*-TEGMA[227] TEGMA-*b*-PFPMA[227] AEMAm-*b*-**354**[236] APMAm-*b*-**354**[236] HPMAm-*b*-DMAPMAm[237] **356**-*b*-HPMAm[239] St-*b*-PFPVS[169] St-*b*-DEAm[234]
 **19** PEO macro-RAFT agent	K*[223]	DMAEMA[223] 2VP-*b*-St[252]
 **20** RAFT inimer	K[253]	St[253]
 **21**	K[254]	**407**[254]
 **22** peptide macro-RAFT agent	K[255]	HPMAm[255]
 **23** RAFT inimer	K[256]	C[256]

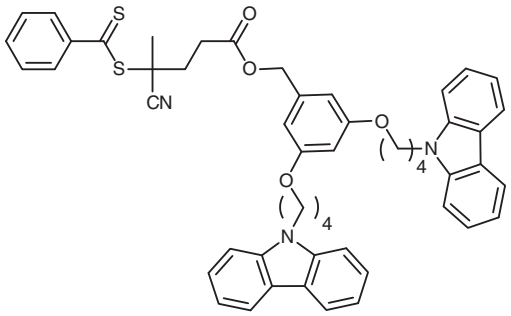
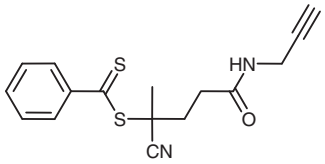
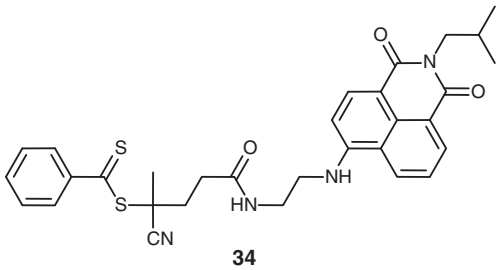
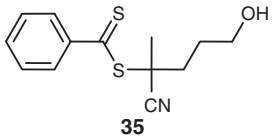
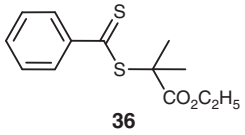
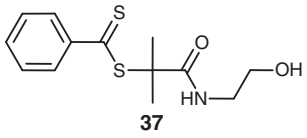
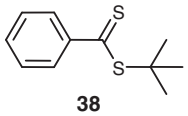
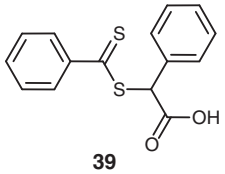
(*Continued*)

Table 3. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **24**	*	HPMAm[238] C[241,257,258]
 **25**	*	tBMA[259] DEGMA[259]
 **26**	K[241]	MA[241]
 **27**	K[241]	MA[241]
 **28**	K*[260]	AEMA[261] TESPMA[260] PEGA-*b*-TMSPA/**339**[262]
 **29**	*	2VP[260]
 **30**	K[213]	C[213]
 **31**	K[263]	C[263]

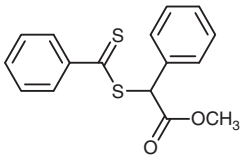
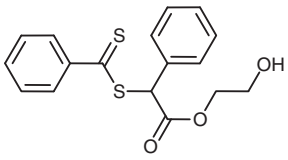
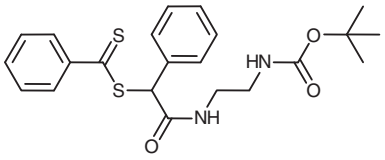
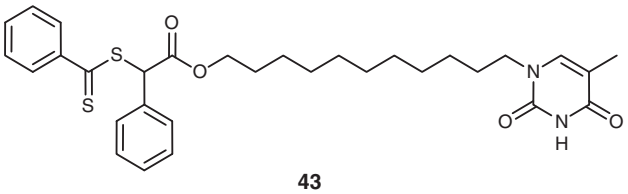
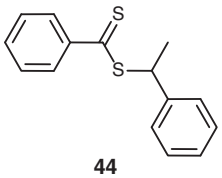
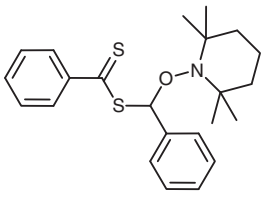
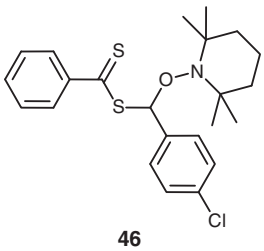
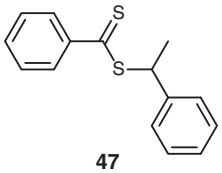
(*Continued*)

Table 3. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **32**	*	[C][264]
 **33**	O[259]	tBMA[259] MMA[259] DEGMA[259]
 **34**	D[265]	HPMA[265] HPMA/NMS[265]
 **35**	*	DMAEMA[266] HA[240] St[267,268]
 **36**	*	(AA/MMA)[269]
 **37**	*	NIPAm/DMAm[270–272]
 **38**	*	DEAm[273] (VAc)[274] (NVP)[248] *EHA-b-MA*[275]
 **39**	*	HA[240]

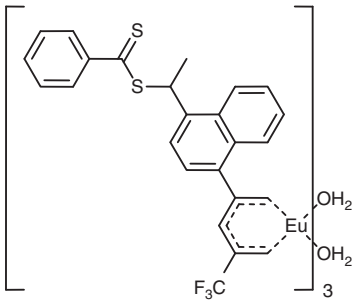
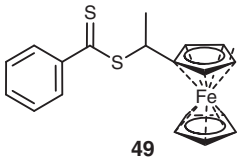
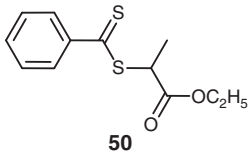
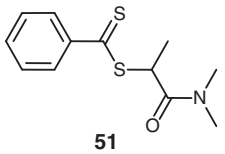
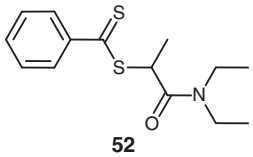
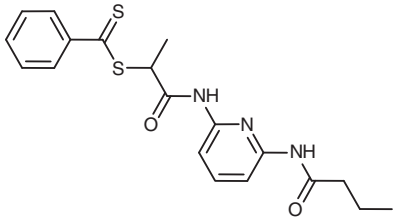
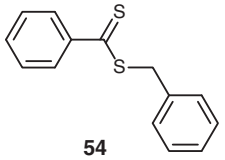
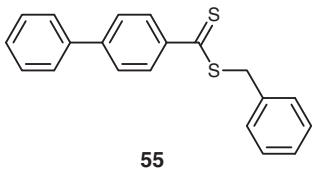
(*Continued*)

Table 3. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **40**	*	HA[240] MMA/**433**[276] MMA/**434**[276] MMA/**435**[276] MMA/**436**[276] MMA/**437**[276] DMAEMA/**433**[276] DMAEMA/**434**[276] DMAEMA/**434**[276] DMAEMA/**437**[276] HEMA/**433**[276] HEMA/**434**[276] HEMA/**434**[276] HEMA/**437**[276] MAA/PEGMA[277] St/CMS[278]
 **41**	A[240]	HA[240]
 **42**	A[240]	HA[240]
 **43**	A[279]	MMA[279]
 **44**	*	St[171] (St-*b*-DMAEMA)[171]
 **45**	A[280]	St[280] NIPAm[280] (AA)[280]
 **46**	A[280]	St[280] PEGMA[280] (tBA)[280]
 **47**	A*[281]	St[171] (St-*b*-DMAEMA)[171] PEGA[281]

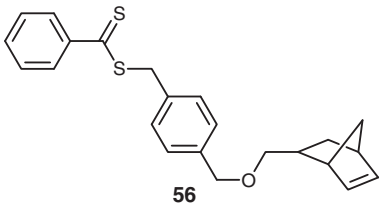
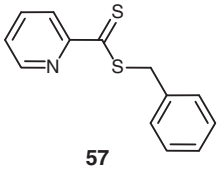
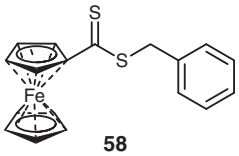
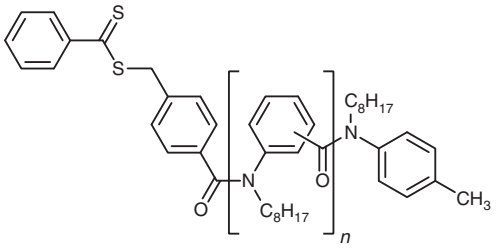
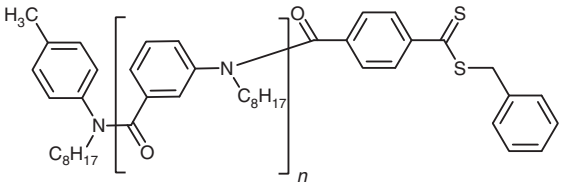
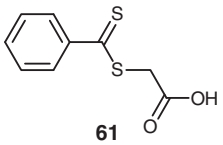
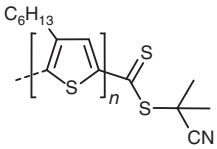
(*Continued*)

Table 3. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **48**	C[282]	MMA[282]
 **49**	A[283]	St[283]
 **50**	A*[122]	BA[122]
 **51**	*	**412**[243]
 **52**	A[284]	DEAm[284]
 **53**	A[285]	BA[285] St[285]
 **54**	*	St[132,286] PFPVS[169] PVS[169] **381**[287] (**382**)[287] **414**[288] BA[286] **364**[289] (VAc)[274] (NVP)[248] (NES)[290] (BES)[290] MAA/EGDMA[291] (PFPVS-*b*-PS)[169] (**399**-*b*-EA)[288] **364**-*b*-**387**[289]
 **55**	*	tBA[292] **368**[292] tBA-*b*-**368**[292]

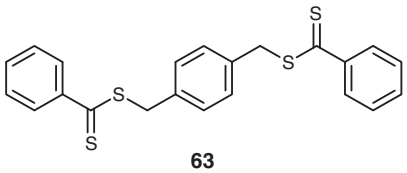
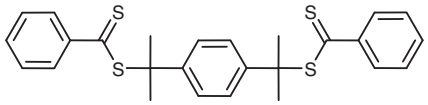
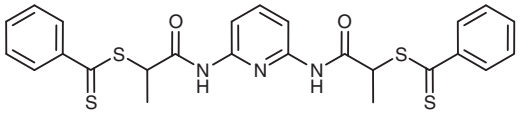
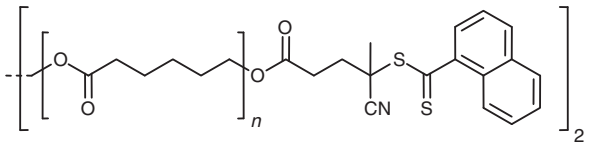
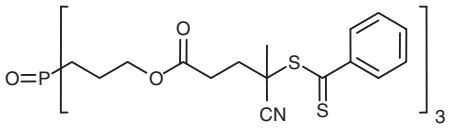
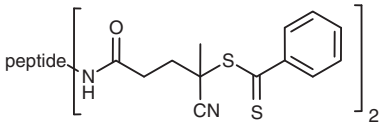
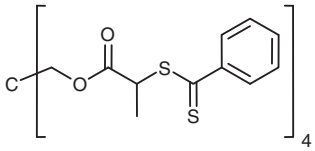
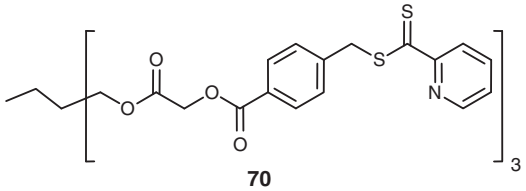
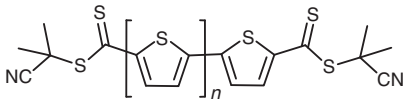
(*Continued*)

Table 3. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **56**	A[293]	St[293]
 **57**	*	iBoA[268,294–296] **351**[297] St[298]
 **58**	A[283]	St[283]
 **59** polybenzamide macro-RAFT agent	A[299]	St[299]
 **60** polybenzamide macro-RAFT agent	A[299]	St[299]
 **61**	*	HA[240] (NIPAm)[300] (NIPAm-*b*-NAS)[300] St/DVB[301]
 **62** poly(3-hexylthiophene) macro-RAFT agent	D[302]	MMA[302]

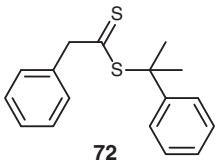
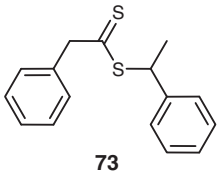
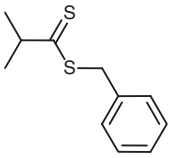
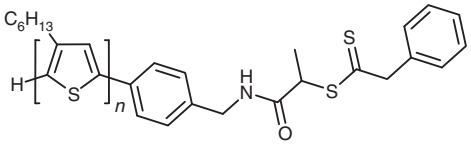
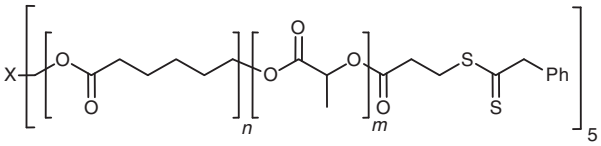
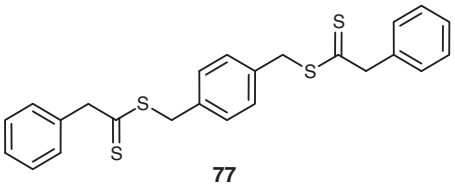
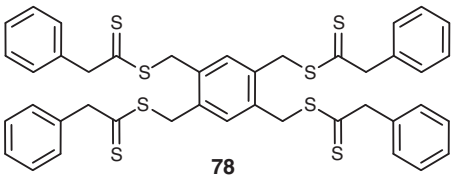
[A]References in this column (where given) are to the synthesis of the RAFT agent. The letter indicates (A–N) the method(s) used (see section on *Synthesis of RAFT Agents* below). An asterisk indicates that the RAFT agent is mentioned in our previous reviews[17–19] or has been previously described.
[B]See section entitled *Abbreviations* for definitions of abbreviations used. If the monomer(s) appear in italics, the polymerization was performed in heterogeneous media (emulsion, miniemulsion, dispersion). If the monomer(s) appear in parentheses, a relatively broad molar mass distribution ($Đ > 1.4$), significant retardation/inhibition and/or other issues were encountered. This does not necessarily indicate an absence of control and the original paper should be consulted for further details. Polymerizations of monomers A and B leading to statistical copolymers are designated as A/B. Polymerizations leading to block copolymers are designated as A-*b*-B. The first mentioned monomer (A) was polymerized first, and the polymer formed was used as a macro-RAFT agent in polymerization of the second mentioned monomer (B).
[C]Compounds not used as RAFT agents directly but served as precursors to other (macro)RAFT agents.

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

RAFT agent	Synthesis[A]	Polymerizations[B]
'R'-connected		
 **63**	*	St[303]
 **64**	*	DMAEMA[304] TFEMA[304] **290**[305] **290**-*b*-**304**[305]
 **65**	A[279]	St[279]
 **66** PCL macro-RAFT agent	K[306]	DMAEMA[306]
 **67**[214]	K[214]	C[214]
 **68** peptide macro-RAFT agent	K[307]	HPMAm[307]
 **69**	A[308]	294[308]
 **70**	H/K[309]	C[309]
'Z'-connected		
 **71** (*n* = 1, 2, 3)	D[302]	MMA[302] S[302]

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

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

RAFT agent	Synthesis[A]	Polymerizations[B]
 **72**	*	(MMA)[310] MA[182] BA[182] **348**[311] B/AN[312]
 **73**	*	St[313,314] BD[315] NIPAm[316] St/MAH[313] *St*[315] *St*-b-(St/*BD*)[314,315] St-*b*-(St/MAH)[313] ((St/MAH)-*b*-St)[313]
 **74**	*	MAA/EGDMA[291]
 **75** poly(3-hexylthiophene) macro-RAFT agent	A[317]	**340**[317]
 **76** *star*-PCL-*b*-PLA macro-RAFT agent	L[318]	NIPAm[318]
 **77**	A*[319]	St[319]
 **78**	*	St[319]

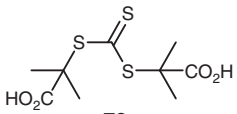
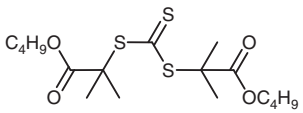
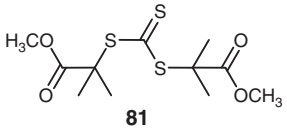
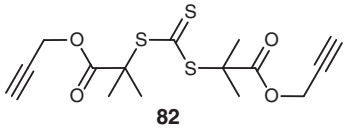
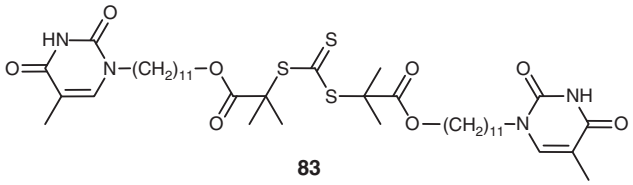
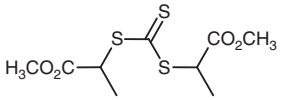
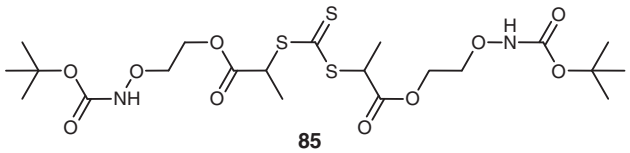
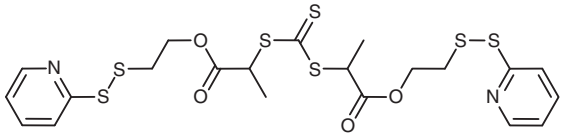
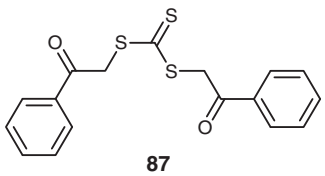
[A]See footnote A of Table 3.
[B]See footnote B of Table 3.

Dithiocarbamates and Switchable RAFT Agents

RAFT polymerization making use of dithiocarbamate RAFT agents are shown in Tables 11–13. Cyanomethyl *N*-methyl-*N*-phenyldithiocarbamate (**258**) is commercially available from Aldrich[20] and Strem.[21] In recent work, it has been used for controlling the polymerization of VAc[366] and VC.[529]

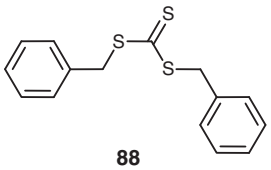
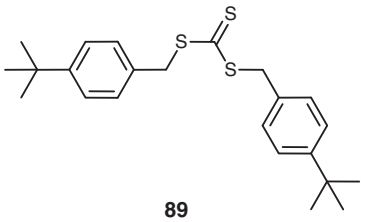
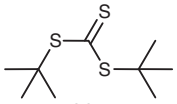
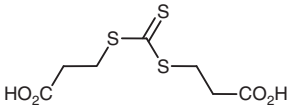
Further details of RAFT polymerization using 'switchable' RAFT agents that can be switched to offer good control over polymerization of both MAMs and LAMs and a route to poly-MAM-*b*-polyLAM has been reported.[530–532] *N*-(4-Pyridinyl)-*N*-methyldithiocarbamates (**275**–**279**) are effective with LAMs and the corresponding *N*-(4-pyridinium)-*N*-methyldithiocarbamates

Table 6. RAFT agents and RAFT polymerizations – Symmetric trithiocarbonate RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B]
 **79**	I*[321,322]	MMA[323] *MMA*[324] AA[325] DMAm[326] (*DMAm*)[326] NIPAm[321] AA/St[327] NIPAm/**361**[328] NIPAm/**362**[328] MAA/CHAm/NIPAm[328] MAA/BzAm/NIPAm[328] MAA/OAm/NIPAm[328] MAA/NIPAm/**361**[328] AA/St-*b*-NVP[327] MAA/NIPAm/**362**[328] MMA-*b*-(PEGMA/NIPAm)[323] (NVP-*b*-MMA)[329,330]
 **80**	I/M[285]	St[285] BA[285]
 **81**	A[320,331]	MMA[320] AN[331]
 **82**	M*[332,333]	C[332,333]
 **83**	M[285]	St[285] Ip[285] BA[285]
 **84**	A*[331]	AN[331] MA[117]
 **85**	K[334]	PEGA[334]
 **86**	K[334]	PEGA[334]
 **87**	*	St[107]

(*Continued*)

Table 6. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **88**	A*[331,335]	CMS[336] St[182,337–339] tBS[337] AN[331] BA[182,274] DMAEA[221] MA[182] iBoA[182] tBA[182] ODA[337] 2EHA[337] PEGA[340] NVP[248] (VAc)[274] B/AN[312] DVE/MAH[341,342] PEGA-*b*-CIPEA[340] ODA-*b*-NIPAm[337] 2EHA-*b*-NIPAm[337] St-*b*-NIPAm[337] tBS-*b*-NIPAm[337] (BA-*b*-VAc)[274] DVE/MAH-*b*-St[341,342]
 **89**	A[343]	*DMAm*[343] *DEAm*[343]
 **90**	*	**346**[344] VAc[274] (NVP)[248] **346**-*b*-**347**[344] (VAc-*b*-BA)[274]
 **91**	*	(St)[107]

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

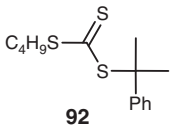
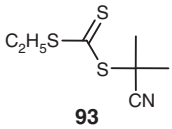
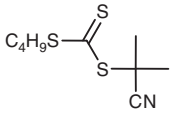
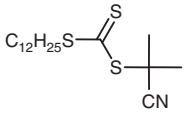
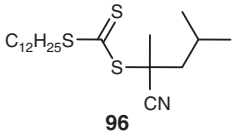
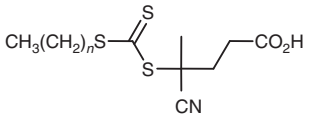
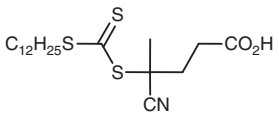
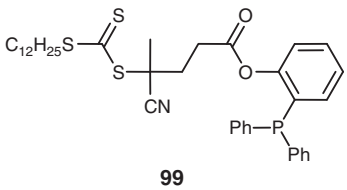
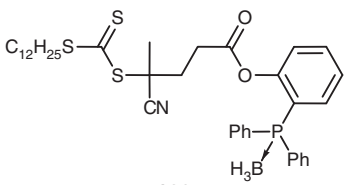
(**275**-H$^+$–**279**-H$^+$) provide excellent control over the polymerization of MAMs (Table 13). In applying the RAFT agents in preparing polyMAM-*b*-polyLAM, the block comprising MAMs needs to be synthesized first. This sequence is necessary because, polyLAM$^\bullet$ are poor homolytic leaving groups with respect to polyMAM$^\bullet$ and, consequently, polyLAM-derived macro-RAFT agents have very low transfer coefficients in MAM polymerization. Attempts to synthesize poly(St)-*b*-poly(VAc) or other poly(St)-*b*-poly(LAM) starting from a poly(St) macro-RAFT agent gave no significant yield of polymer for an extended period (>4 h) corresponding to the time needed to convert the initial macro-RAFT agent.[530,531] This can be attributed to the very low rate of poly(St)$^\bullet$ addition to VAc, possibly compounded by the presence of trace amounts of St monomer in the poly(St) macro-RAFT agent. A solution to this difficulty lay with forming an intermediate 'block' of poly(MA).[530,531]

There has been recent emphasis on RAFT polymerization in aqueous media for a variety of reasons which include: (i) perceived environmental benefits, (ii) control over polymerization of monomers with cationic, anionic, zwitterionic, and neutral polar groups which have limited solubility in organic media, and (iii) the need to perform polymerization under physiological conditions. Switchable RAFT agents have been proven effective in the aqueous solution polymerization of *N*,*N*-dimethylacrylamide (DMAm).[532] A quantitative study of the influence of acid type and concentration was performed for the polymerization of DMAm.[532] The conclusion was that best control over MAMs is achieved with stoichiometric amounts of a strong acid (e.g. toluenesulfonic acid). The polymerizations were performed with the tetraethyleneglycol macro-RAFT agent **279** which provided enhanced water solubility for the initial RAFT agent in its neutral (unswitched) form.

Polymerizations of LAMs (specifically NVP) in water with the switchable RAFT agents were complicated by the inherent instability of the NVP-based macro-RAFT agents in aqueous media aggravated by the presence of even trace amounts of acid.[532] The recent work of Destarac and co-workers suggests that this problem might be overcome with room temperature polymerization.[506,507] Block copolymers with LAMs were successfully prepared from the DMAm macro-RAFT agent in organic solution.

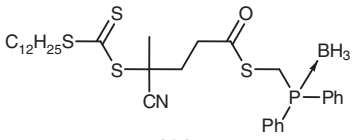
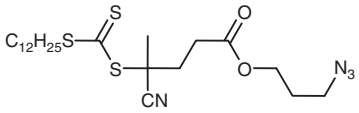
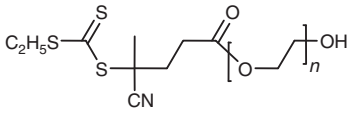
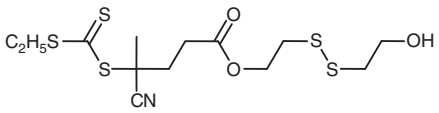
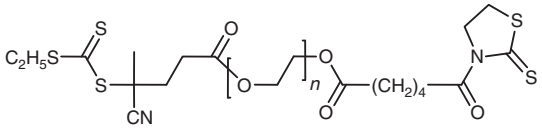
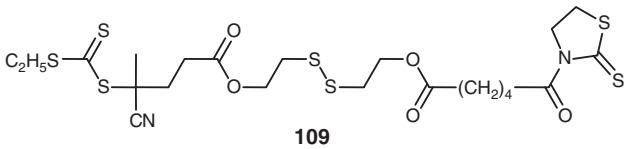
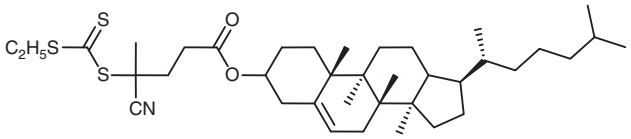
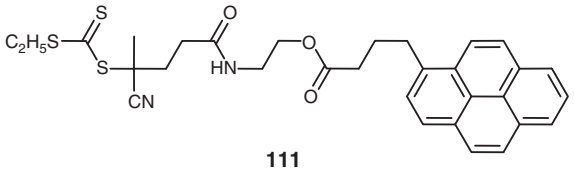
The *N*-aryl-*N*-(4-pyridinyl) dithiocarbamates (**273**, **274**) are more effective (dispersities are lower) than the analogous *N*-(4-pyridinyl)-*N*-methyldithiocarbamates (**278**) with LAMs (NVC, VAc) in the unswitched (neutral) form and more active with MAMs (MA) in their switched (protonated) form.[115] Activity, as indicated by a higher C_{tr}^{app} or a lower $Đ$ for the polymer formed, increases with the electron-withdrawing qualities of Ar–X. Some retardation was also observed with the more active RAFT agents of this class.

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

RAFT agent	Synthesis[A]	Polymerizations[B]
 **92**	D*	NPMI/Lim[345]
 **93**	D*	**359**[170]
 **94**	A[346] D*	MMA[346] St[194] **376**[347] **378**[347] **379**[347] BA[194] NPMI/Lim[345] **376**-*b*-**378**[347] **376**-*b*-**379**[347] **378**-*b*-**376**[347]
 **95**	*	MMA[21] **303**[209] St[109,132] NIPAm[109]
 **96**	D[348]	DMAm[348] DMAm-*b*-HEAm[348]
 **97** n = 1 or 2	D*[349,350]	DEAEMA[351] DMAEMA[350,352] PEGMA[224,353–355] (**412**)[243] PAA[356] DMAm[326] *DMAm*[326] HPMAm[357] **357**[357] MAA/PEGMA[354] APMAm/DEAPMAm[358] APMAm/DMAPMAm[358] DEAEMA-*b*-NIPAm[351] DMEAEMA-*b*-NIPAm[359] *PEGMA/MAA-b-St*[354,360] *PEGMA/MAA-b-BzMA*[361] *PEGMA/MAA-b-**327***[362] PAA-*b*-DMAm/**408**[356] DMAEMA-*b*-(PAA/BMA/DMAEMA)[350,352] HPMAm/**450**/**451**[363] HPMAm-*b*-**357**[357]
 **98**	*	CMA[364] **317**[311] **332**[365] **333**[365] DMAm[366] BA[366] **350**[311] NIPAm[366,367] MAA/MMA[368] MAA/DFHA[369] OeMA/MMA[364] **332**-*b*-MMA[365] **333**-*b*-MMA[365] NIPAm-*b*-DMAEAm[367]
 **99**	K[370]	S[370]
 **100**	K[370]	S[370]

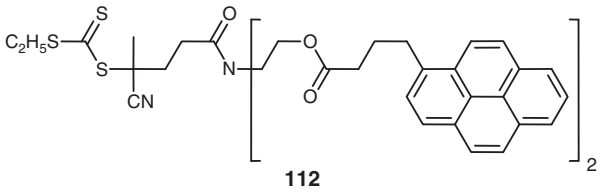
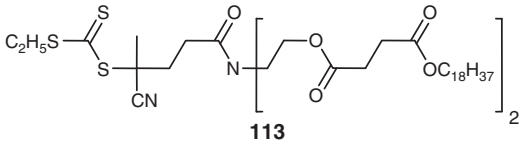
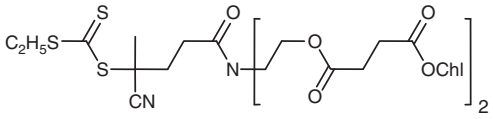
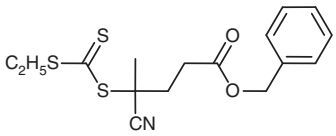
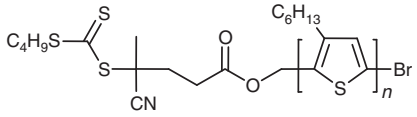
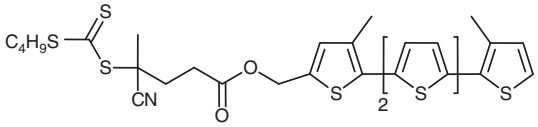
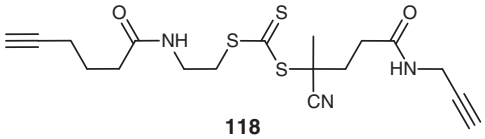
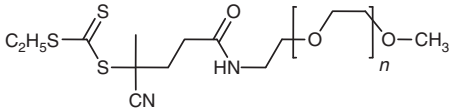
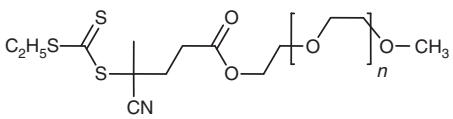
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **101**	O[370]	S[370]
 **102**	*	MAA[371]
 **103** $n = 2$	K[372]	HPMAm[372] PEGMA[373]
104 $n = 4$	K[374]	PEGMA[374]
105 n = polymer	K[375]	*PEGMA*[224]
 **106**	K[376]	HPMAm[376]
 **107** $n = 2$	K[372]	HPMAm[372] PEGMA[373]
108 $n = 4$	K[374]	PEGMA[374]
 **109**	K[376]	HPMAm[376]
 **110**	D[349]	PEGA[349]
 **111**	D[257]	DMAm[257]

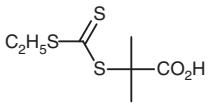
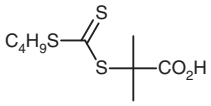
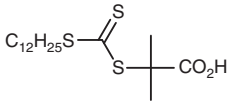
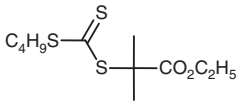
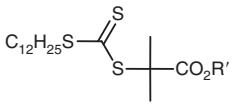
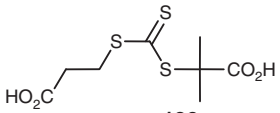
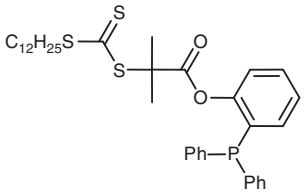
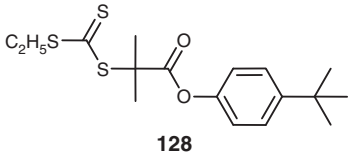
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **112**	D[257]	DMAm[257] DMAm/NAS[257]
 **113**	D[257]	DMAm[257]
 **114** (Chl = cholesteryl)	D[257]	DMAm[257] HPMAm[257] DMAm/NAS[257]
 **115**	D[377]	DEGMA[377] PEGMA[377]
 **116** poly(3-hexylthiophene) macro-RAFT agent	D[378]	St[378]
 **117**	D[378]	MMA[378] St[378] AA[378] MA[378]
 **118**	D[379]	HPMAm[379]
 **119** PEO macro-RAFT agent	D[380]	APMAm[380] APMAm-*b*-NIPAm[380]
 **120** PEO macro-RAFT agent	D*[381]	*St*[381]

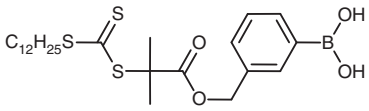
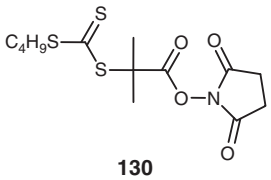
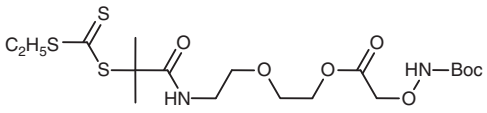
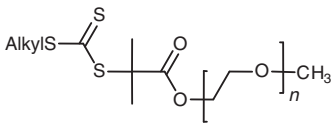
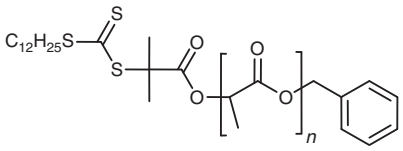
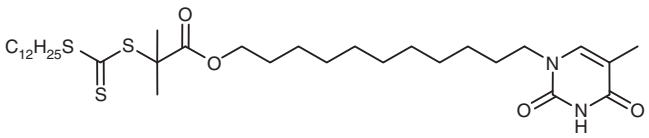
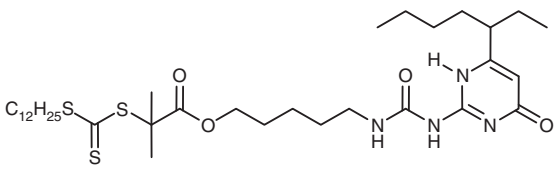
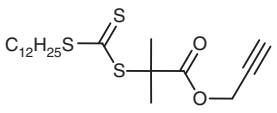
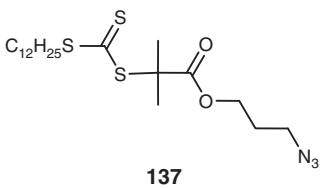
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **121**	I*	MA[375] (**412**)[243] DMAm[375] DMAm[326] *DMAm*[326] St[375] NIPAm[375,382] DMAm-*b*-**370**-*b*-**365**[383]
 **122**	A[346,384] I[385,386]	CHMA[384] MMA[346] **300**[387]
 **123**	I*[388]	**306**[389] DMAm[326,390–392] (*DMAm*)[326] St[370] *St*[393] PFS[200] 4VP[200,394] **390**[395] Ip[396] **394**[396] AA[397] NIPAm[367,392,398] NVC[387] (NVP)[399] PAA/NIPAm[189] AA/PEGA[234,400] (tBMA/DMAEMA/**290**)[175] HEA/PEGA[401] PA/PEGA[401] AA-*b*-St[393] St/**406**[402] HEMA/Ip[396] HEA/Ip[396] Ip/**394**[396] AA/PEGA-*b*-**343**[234] *AA/PEGA*-b-*St*[400] DMAm/**296**[390] DMAm/PFS[169] **306**-*b*-St[389] HADA/MADA/NLAA[403] HADM/MADM/NLAM[403] *AA/PEGA-b-**344***[362] *AA-b-St*[397] DMAm-*b*-NIPAm[390] DMAm/**296**-*b*-NIPAm[390] DMAm-*b*-NIPAm/**296**[390] DMAm/**296**-*b*-NIPAm/**296**[390] NIPAm-b-DMAEAm[367] PFS-*b*-PFPVS[169] 4VP-*b*-PFS[200] *4VP-b-St*[394] DMAm-*b*-MA[392] DMAm-*b*-BA[392] DMAm-*b*-NIPAm[392] NIPAm-*b*-MA[392] NIPAm-*b*-BA[392] NIPAm-*b*-DMAm[392] (NVP-*b*-Ip)[399]
 **124a** R′ = butyl	A[346]	MMA[346]
 **125** R′ = butyl Lubrizol CTA-1	I[159,160]	–
 **126**	I*	St[107] *AA/Am*[404] *Am-b-AA*[404]
 **127**	K[370]	St[370]
 **128**	K[343]	*DEAm*[343] *DMAm*[343] *NIPAm*[343]

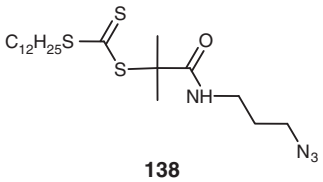
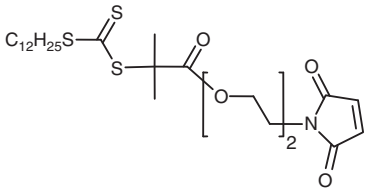
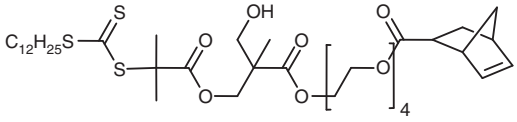
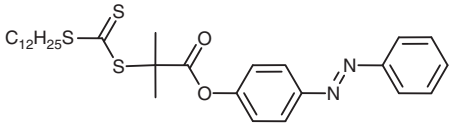
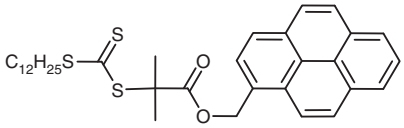
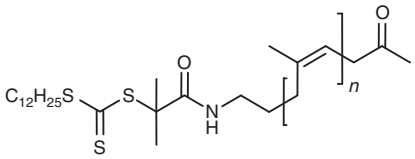
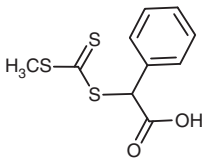
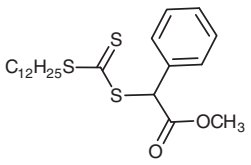
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **129**	I[405]	DMA[405] St[405] DMA-*b*-NIPAm[405] St-*b*-DMA[405]
 **130**	G[386]	[C][406,407] NIPAm[386]
 **131**	G[408]	NIPAm[408]
 **132** PEO macro-RAFT agent	Alkyl = C_2H_5 G*[381,409] Alkyl = C_4H_9 G[385] Alkyl = $C_{12}H_{25}$ G[410]	BA[385] EHA[385] NIPAm[411] *St*[381,410] **390**[395] DEGMA/PEGMA/**309**[409] BA-*b*-**334**[385] EHA-*b*-**334**[385]
 **133** PLA macro-RAFT agent	G[412]	**377**[412] St/**386**[413] St/HEMA[414] St/HEA[414]
 **134**	G[279]	IP[279]
 **135**	G[415]	MMA[415] St[415] MA[415] tBA[415] NIPAm[415] DMAm[415] MA-*b*-tBA[415] MA-*b*-DMAm[415]
 **136**	G*[388,416]	**310**[417] St[418] 4VP[388] BA[416] tBA[416] EHA[416] LA[416] PEGA[416] NIPAm[267]
 **137**	G*	**395**[371]

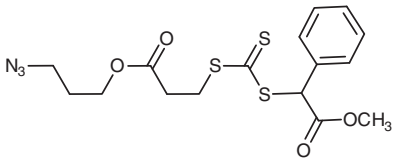
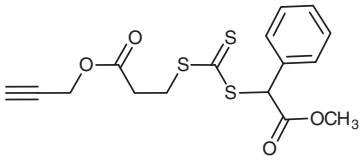
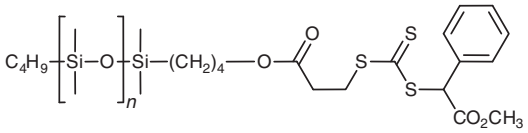
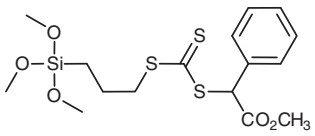
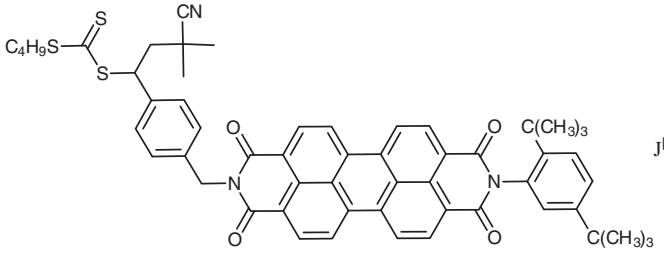
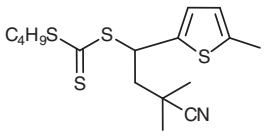
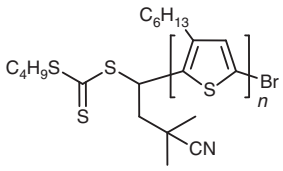
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **138**	G[419]	NIPAm[419]
 **139**	*	C[420]
 **140**	K[421]	St[421]
 **141**	K[422]	DMAm-*b*-NIPAm[422]
 **142**	K[423]	DEAEMA[423] DEAEMA/**367**[423]
 **143** polyisoprene macro-RAFT agent	L[424]	tBA[424]
 **144**	A[425]	C[425] MPC[426] MPC-*b*-DMAEMA/NIPAm[426]
 **145**	A[427,428]	**341**[428] **355**[427] St[428] (St/**341**)[428] (**341**-*b*-St)[428] St-*b*-**341**[428]

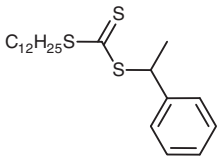
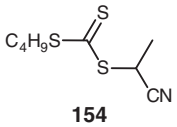
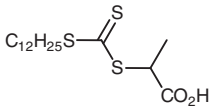
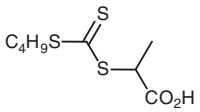
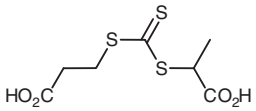
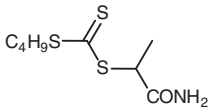
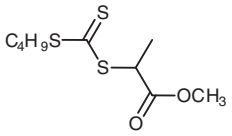
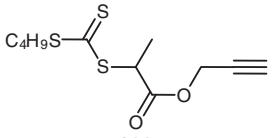
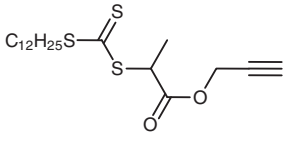
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **146**	K[429]	MMA[429] St[429] NIPAm[429]St-*b*-**335**[429] St-*b*-NIPAm[429] St-*b*-NAM[429] St-*b*-tBA[429] St-*b*-NAM-*b*-NIPAm[429] St-*b*-NAM-*b*-DMAm[429] St-*b*-**335**-*b*-MA[429] St-*b*-NAM-*b*-NIPAm-*b*-tBA[429] St-*b*-NAM-*b*-DMAm-*b*-tBA[429]
 **147**	K[430]	(MMA)[430] St[430] MA[430] tBA[430] DMAm[430] St-*b*-MA[430] St-*b*-NAM[430] St-*b*-NIPAm[430] St-*b*-DMAm[430] St-*b*-**290**[430] St-*b*-NAM-*b*-MA[430] St-*b*-NIPAm-*b*-MA[430] St-*b*-DMAm-*b*-MA[430] St-*b*-**290**-*b*-MA[430]
 **148** PDMS macro-RAFT agent	K[431]	*MMA*[431]
 **149**	*	MMA[432] St[432] BA[432] MA[432] DMAm[432] NAM[432] NIPAm St-*b*-MA[432] St-*b*-DMAm[432] St-*b*-NAM[432] St-*b*-NIPAm[432] St-*b*-NAM-*b*-tBA[432] St-*b*-NAM-*b*-MA[432] St-*b*-NAM-*b*-DMAm St-*b*-NAM-*b*-NIPAm[432] St-*b*-NIPAm-*b*-MA St-*b*-NAM-*b*-tBA-*b*-MA[432] St-*b*-NAM-*b*-DMAm-*b*-MA[432] St-*b*-NAM-*b*-NIPAm-*b*-MA[432]
 **150**	J[433]	**376**[433] **380**[433]
 **151**[433]	J[433]	St[433]
 **152**[433] poly(3-hexylthiophene) macro-RAFT agent	J[433]	St[433]

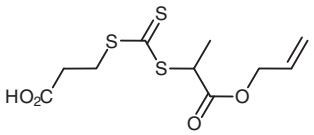
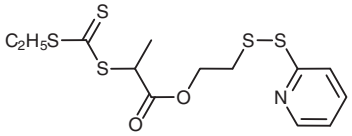
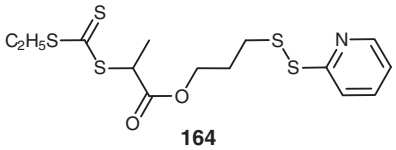
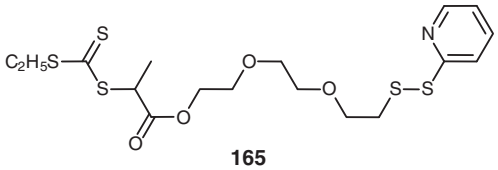
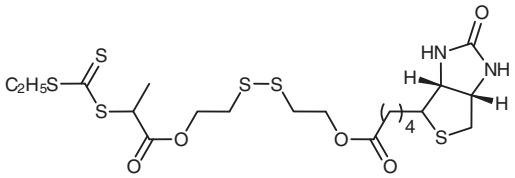
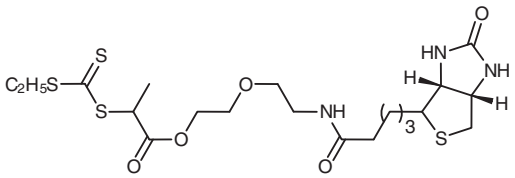
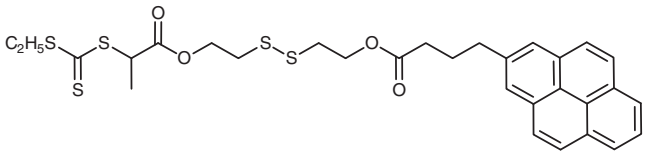
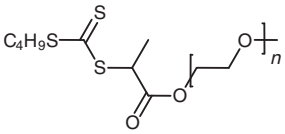
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **153**	A[434]	St/**392**[434] St/**392**-*b*-NIPAm[434]
 **154**	A[384]	CHMA[384]
 **155**	A*[435]	St[221] CMS[436] (BD)[437] (Ip)[437] AA[438] BA[221,439] **348**[311] (DMAEA)[221] (DADMAC)[440] AN/BD[312] (AN/BD)[441] St/MAH[435] (*AA-b-TFEMA*)[438] AA-*b*-St[437] (AA-*b*-St-*b*-BD)[437] (AA-*b*-St-*b*-Ip)[437] (*AA*-b-*St*-b-*Ip*)[437] (*AA*-b-*BA*-b-*St*-b-*BD*)[437]
 **156**	A*	St[192] AA[207] AA/BA[325] AA/PEGA[207] St-*b*-St/**413**[192] AA-*b*-PEGA[207] DMAm[442] DMAm-*b*-St[442]
 **157**	A*	St[107]
 **158**	A[443]	BA[443]
 **159**	*[444]	tBA[445] DMAEA[444] NIPAm[446] **369**[445] NIPAm[445] **411**[445]
 **160**	A[442,447]	HEA[448] tBA[442] CMS[447] CMS-*b*-St[447] tBA-*b*-St[442] DMAm[442] DMAm-*b*-St[442]
 **161**	A[449]	AN/BD[449]

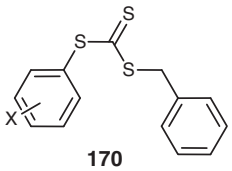
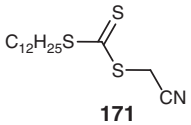
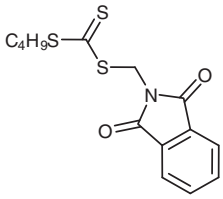
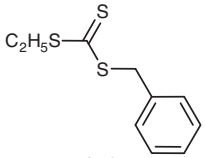
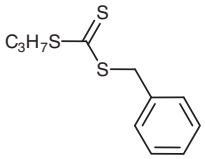
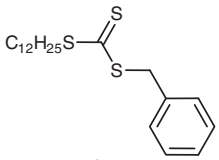
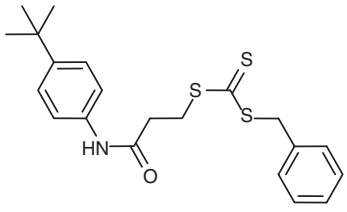
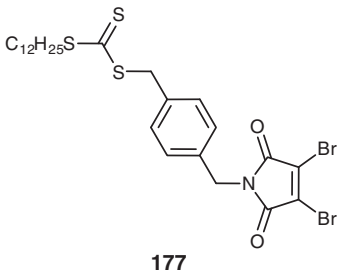
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **162**	A[450]	NIPAm[450]
 **163**	K[451]	**393**[451]
 **164**	*	PEGA[452] NIPAm[453]
 **165**	K[451]	**393**[451]
 **166**	K[454]	NIPAm[454]
 **167**	K[454]	NIPAm[454]
 **168**	A[455]	NIPAm[455] DMAEA[456] AA[456]
 **169** PEO macro-RAFT agent	A[207]	AA[207]

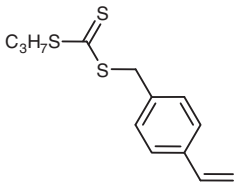
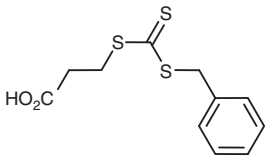
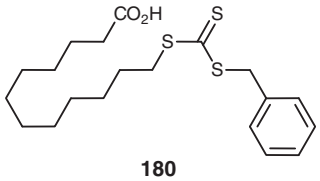
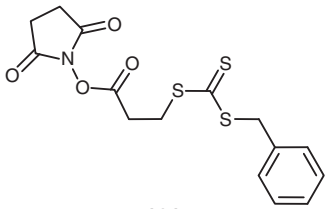
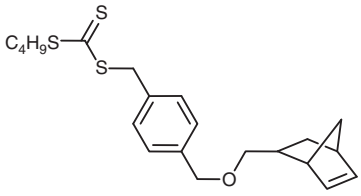
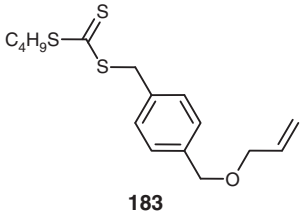
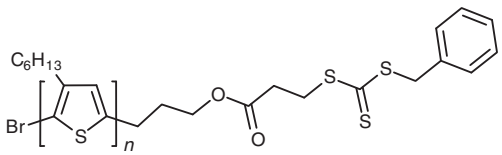
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **170**	B[108]	St[108]
 **171**	A*	(iPOx)[191] BA[21]
 **172**	A*	AA/PA[457]
 **173**	*	PEGMA-*b*-EGMA[355] DMAm[355]
 **174**	A*	BA[124]
 **175**	A*	St[108] *St*[458]
 **176**	A[343]	*DEAm*[343] *DMAm*[343]
 **177**	A[459]	St[459] MA[459] tBA[459] TEGA[459] NIPAm[459]

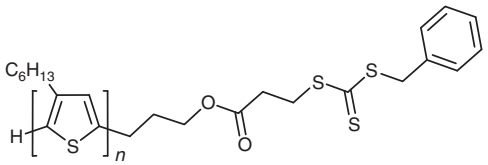
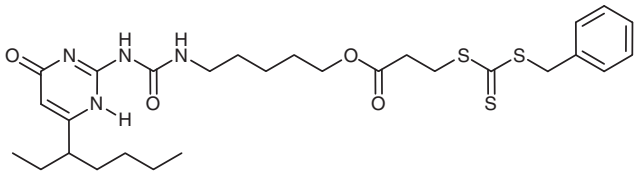
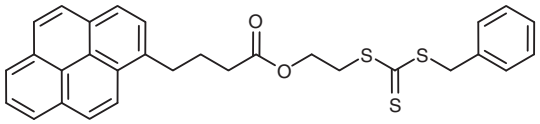
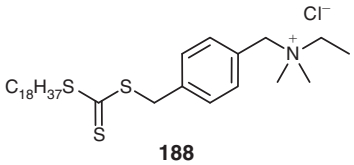
(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **178** RAFT inimer	A[460]	(**178**/MA)[460] (**178**/tBA)[460] (**178**/MMA)[460] (**178**/St)[460] (**178**/MA-*b*-tBA)[460] (**178**/MA-*b*-St)[460]
 **179**	A*	PEGA[461,462] PFPA[463] tBA[461] NIPAm[220,461,464] NIPAm/**372**[464] NIPAm/**391**[465]
 **180**	A	St[303]
 **181**	A[466]	C[466]
 **182**	A[293]	MA[293] EEA[293] St[293]
 **183**	A[293]	St[293]
 **184** poly(3-hexylthiophene) macro-RAFT agent	A*[467]	4VP[467]

(*Continued*)

Table 7. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **185** poly(3-hexylthiophene) macro-RAFT agent	A[468]	St[468]
 **186**	A[415]	St[415]
 **187**	A[469]	**373**[469] **374**[469] **375**[469] St/**383**[470] St/**384**[470,471] **374**-*b*-**375**[469]
 **188**	A[472]	NIPAm[472] NIPAm-*b*-tBA[472,473]

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

Other RAFT Agents

Other RAFT agents, namely those with Z = sulfonyl, phosphonate, or phosphine, are shown in Table 14.

The RAFT agents where Z is a strongly electron withdrawing alkyl or phenylsulfonyl group (**280**, **281**) are prone to undergo direct reaction with (meth)acrylate monomers (BA, MA, tBA, and MMA) under polymerization conditions with consumption of the thiocarbonylthio group and ultimately little control over the polymerization.[546] A hetero-Diels Alder mechanism was suggested. Good control was achieved only for iBoA with **280** where the side reactions with monomer were suppressed by steric factors due to the bulky ester substituent.[546,547]

RAFT Agent Selection

Monomers can be considered as belonging to one of two broad classes. The 'more-activated' monomers (MAMs) are those where the double bond is conjugated to an aromatic ring (e.g. St, 4VP) a carbonyl group (e.g. MMA, MA, Am) or a nitrile (e.g. AN). The 'less activated' monomers (LAMs) are those where the double bond is adjacent to saturated carbon (e.g. DADMAC), an oxygen or nitrogen lone pair (e.g. VAc, NVP) or the heteroatom of a heteroaromatic ring (NVC).

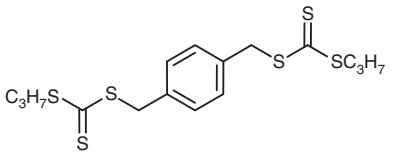
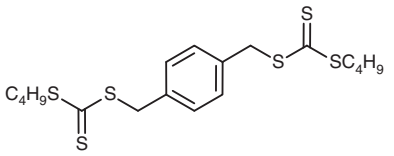
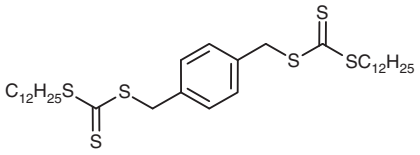
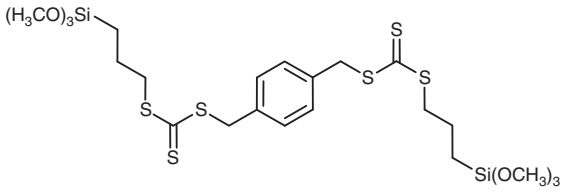
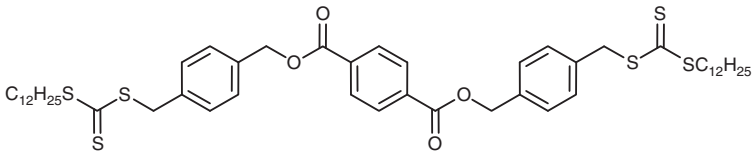
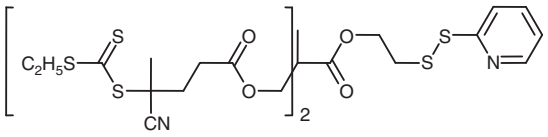
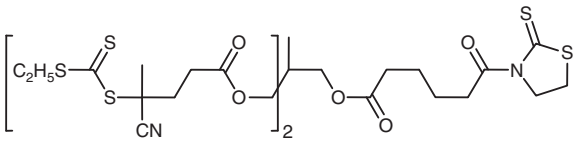
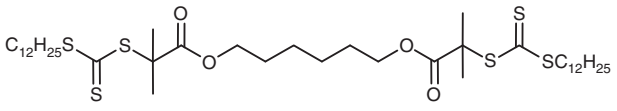
RAFT agents such as dithioesters (Z = aryl or alkyl) or trithiocarbonates (Z = alkylthio) suitable for controlling polymerization of MAMs, inhibit or retard polymerizations of (LAMs). Similarly RAFT agents suitable for controlling polymerizations of LAMs such as *N*,*N*-dialkyl- or *N*-alkyl-*N*-aryl dithiocarbamates and xanthates tend to have low transfer constants and are ineffective with MAMs.

Fig. 4, which is based on that in our previous reviews but is updated to include switchable RAFT agents,[17–19,137,550] provides a general summary of how to select the appropriate RAFT agent for particular monomers. Note should be made of the dashed lines in the chart. Although some control might be achieved with these monomer–RAFT agent combinations, the molar mass distribution may be broad or there may be substantial retardation or a prolonged inhibition period. This proviso has been omitted in some representations of this data in the literature. The data is presented in another form in Table 15.[551] There are several examples that have been reported (see Tables above) which fall outside of these guidelines and where good control (i.e. low dispersities, successful block synthesis) has, nonetheless, been achieved.

Synthesis of RAFT Agents

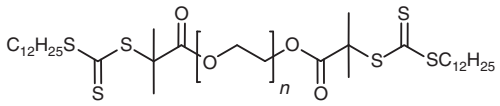
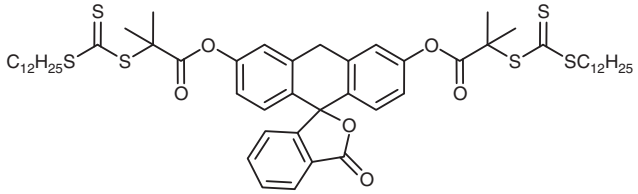
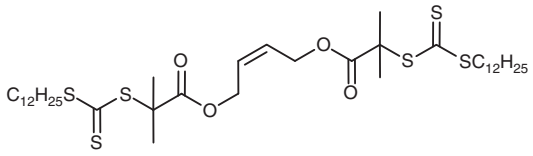
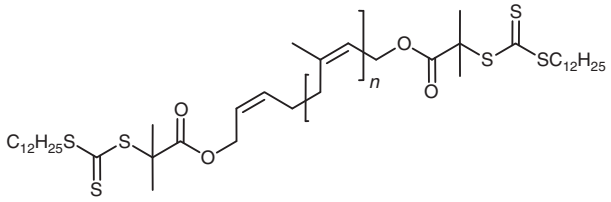
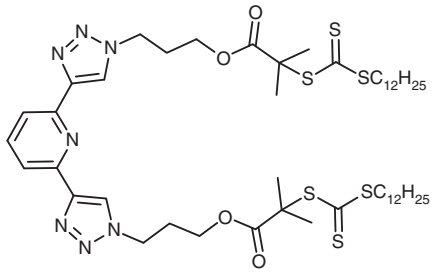
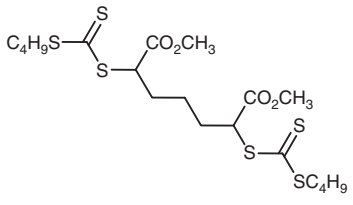
The methods most commonly exploited for the synthesis of (low molar mass) RAFT agents are listed below. The method of choice is dependent on the structure of the desired RAFT agent, the amount required, the toxicity and ease of handling of reagents, and other factors. We have recently completed a

Table 8. Multi-RAFT agents and RAFT polymerizations – Trithiocarbonate RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B]
'R'-connected		
 **189**	A[474]	NIPAm[337]
 **190**	A[475]	BA[311] **349**[311] DMAm[475] DMAm-*b*-NIPAm[475]
 **191**	*	tBA[474] St[303,474]
 **192**	A*[476]	C[476]
 **193**	A[474]	tBA[474] St[474]
 **194**	K[477]	HPMAm[477]
 **195**	K[372]	HPMAm[372] PEGMA[373]
 **196**	N[478]	St[478] St-*b*-MA/ODA[478]

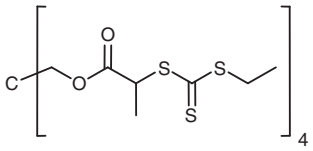
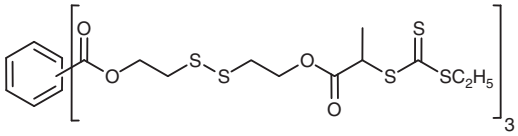
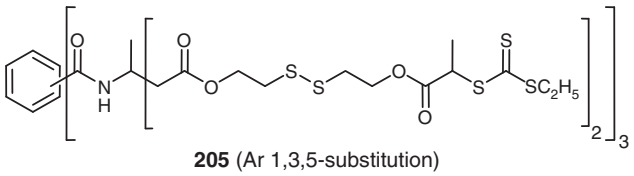
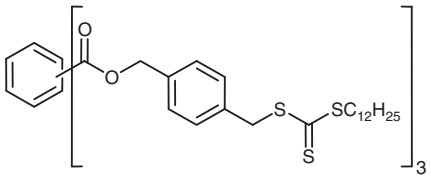
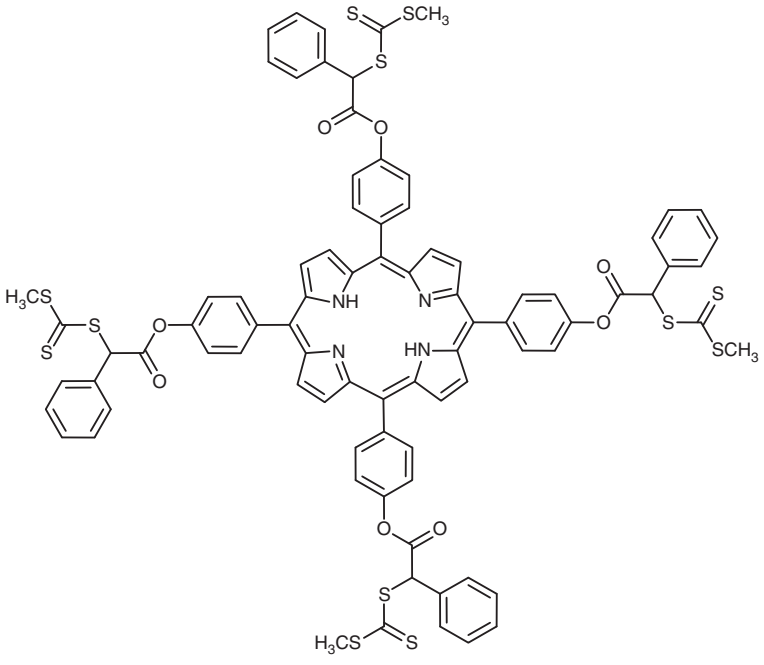
(*Continued*)

Table 8. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **197**	L[479]	NIPAm[479]
 **198**	A[384]	CHMA[384]
 **199**	L[480]	C[480]
 **200** polyisoprene macro-RAFT agent	Q[480]	tBA[480]
 **201**	K[481]	MMA[481] tBA[481] St[481] St-*b*-tBA[481]
 **202**	**A***[482]	tBA[482] tBA-*b*-AA/tBA[482] CIPEA[340] CIPEA-*b*-PEGA[340]

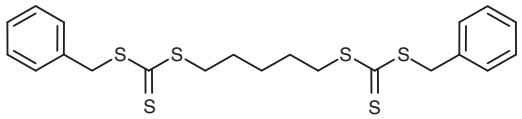
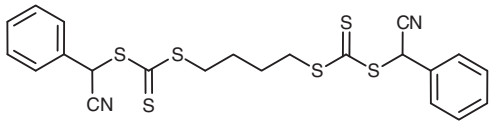
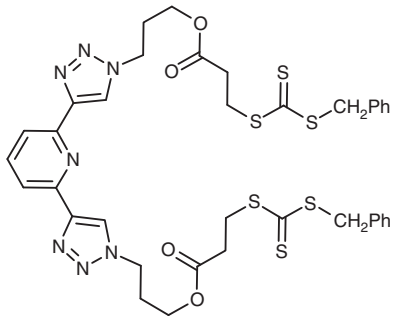
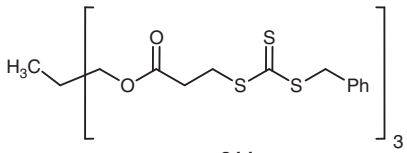
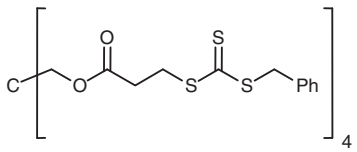
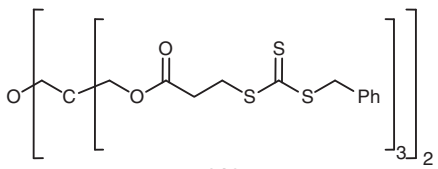
(*Continued*)

Table 8. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **203**	A[483]	NIPAm[483]
 **204** (Ar 1,3,5-substitution)	K[484]	PEGA[484] St[484]
 **205** (Ar 1,3,5-substitution)	K[485]	PEGA[485] St[485] St-*b*-PEGA[485]
 **206** (Ar 1,3,5-substitution)	A[474]	St[474]
	K[425]	DEAm[425]

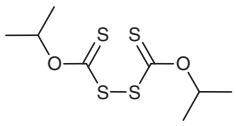
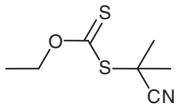
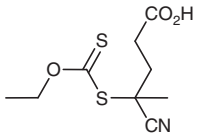
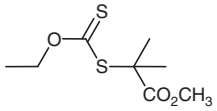
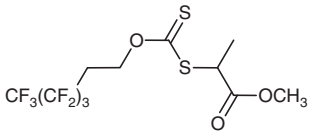
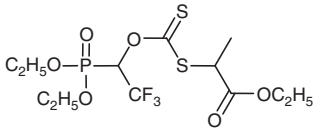
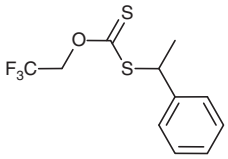
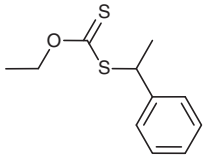
(*Continued*)

Table 8. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
'Z'-connected		
 **207**	A[474]	St[474] tBA[474]
 **208**	A[110]	MMA[110] GMA[110] St[110] MMA-*b*-GMA[110] GMA-*b*-MMA[110]
 **209**	K[481]	St[481] tBA[481]
 **210**	*	C[476]
 **211**	**A***[474]	St[474]
 **212**	**A***[486,487]	St[487,488] THPA[486] THPA-*b*-**366**[486]
 **213**	**A***[486,487]	St[487] THPA[486] THPA-*b*-**366**[486]

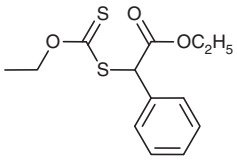
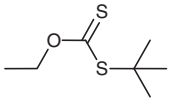
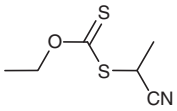
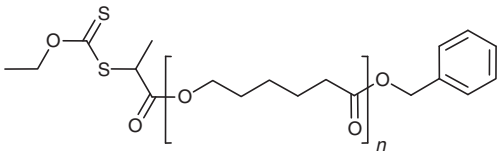
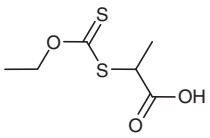
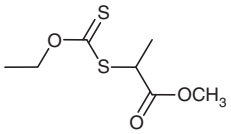
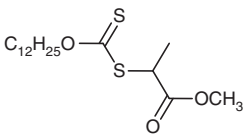
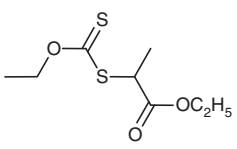
[A]See footnote A of Table 3.
[B]See footnote B of Table 3. In the case of bis-RAFT agents sequential polymerization of two monomers will yield a triblock.
[C]See footnote C of Table 3.
[D]Used in self condensing vinyl polymerization.

Table 9. RAFT agents and RAFT polymerizations – Xanthate RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B]
 **214**	*	VAc[489,490] NVC[489]NVP[489,491] (NVP-*b*-NIPAm)[491] VAc-*b*-VNd[490]
 **215**	D*	NVP[103] NVPI[492]
 **216**	D	NVP[103]
 **217**	A*[493]	NVP[493]
 **218**	A[494]	DMAm[494] VAc[494] DMAm-*b*-VAc[494]
 **219**	A*	BA[125]
 **220**	A*[495]	(*St*)[495]
 **221**	A*	(*St*)[495] (NES)[290] (BES)[290] (NVP)[103] NVC[496] (NVC-*b*-**311**)[496] NVC-*b*-**314**[496]

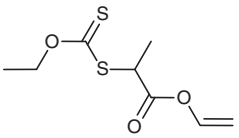
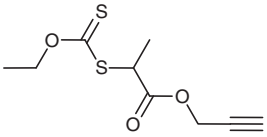
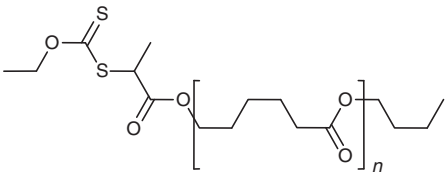
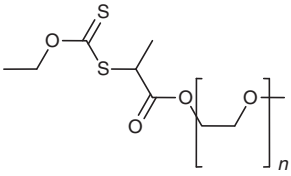
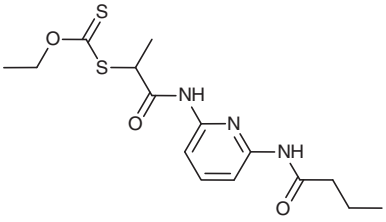
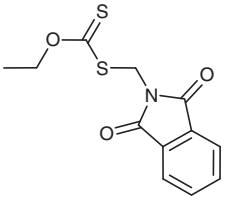
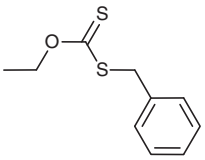
(*Continued*)

Table 9. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **222**	A	NVP[103]
 **223**	G[103]	(NVP)[103]
 **224**	A[103]	NVP[103]
 **225** PCL macro-RAFT agent	A[497]	NVP[497]
 **226**	A*	(NVP)[498] (NVP-*b*-VAc)[498]
 **227** (Rhodixan A1)	A*	(CMS)[336] (AA)[499] *BA*[500,501] NIPAm[499] TMAPAm[499] (DMAm)[494] VAc[494,502,503] VBz[503] VPv[503] NES[290] BES[290] VF2[504] NVC[290] NVCL[505] NVP[506,507] VPA[506,508] (DADMAC)[113,506] (*AA/iBoA*)[509] (*AA-b-iBoA*)[509] VF2/PMVE[504] DMAm-*b*-VAc[494] (PDMAm-*b*-VF2)[504] VAc-*b*-VBz[503] (VAc-*b*-VPv)[503] VBz-*b*-VAc[503] VBz-*b*-VPv[503] VPv-*b*-VAc[503] (VPv-*b*-VBz)[503] NVC-*b*-NES[290] AA-*b*-VPA[508] (Am-*b*-DADMAC)[113] (AA-b-DADMAC)[506]
 **228**	A[501]	(*BA*)[501]
 **229**	A*[103,493]	(*St*)[510,511] (BA)[112] (*BA*)[511] (*MA*)[511] NIPAm[112] VAc[512] VPv[513] NVC[514] NVP[103,493,515] *NVP*[513] NVPip[516] NVC[514,515] VAc/VPv[513] (BA-*b*-St)[511] (MA-*b*-St)[511] BA-*b*-NIPAm[112] NVC-*b*-Ac[514] NVP-*b*-NVC[515] NVPip-*b*-VAc[516] NVC-*b*-NVP[515] NVC-*b*-VAc[514] (NIPAm/NVPI)[517]

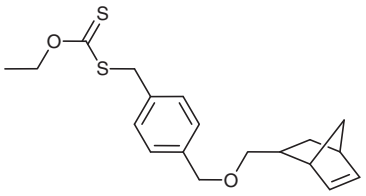
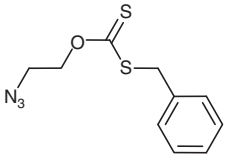
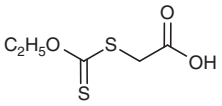
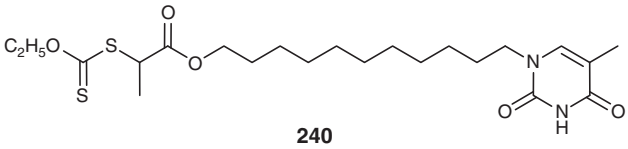
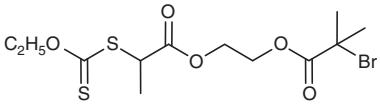
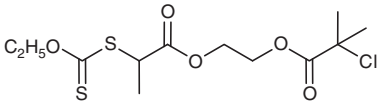
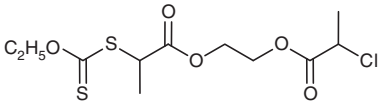
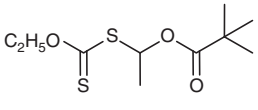
(*Continued*)

Table 9. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **230** RAFT inimer	A[512]	(VAc)[512] (**230**)[512] (**230**-*b*-VAc)[512]
 **231**	A*[518]	VAc[518]
 **232** PCL macro-RAFT agent	A[519]	NVCL[519]
 **233** PEO macro-RAFT agent	*	NVC[514] NVCL[519]
 **234**	A[285]	VAc[285]
 **235**	A*	VAc[520,521]
 **236**	A*	(NES)[290] (BES)[290]

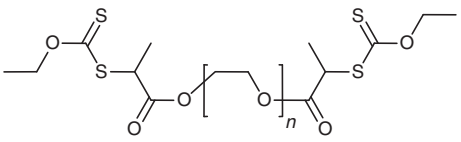
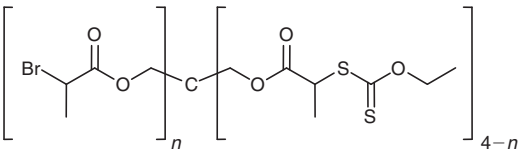
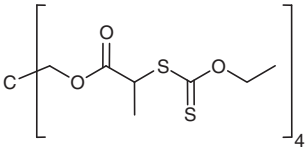
(*Continued*)

Table 9. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **237**	A[293]	VAc[293]
 **238**	A*	VAc[522]
 **239**	A*	VAc[523] VBz[523] VAc-*b*-VBz[523] VAc-*b*-VPv[523]
 **240**	A[524]	VAc[279]
 **241**	A*	(NVP)[525]
 **242**	A[525]	NVP[525]
 **243**	A[525]	NVP[525]
 **244**	A[503]	VAc[503]

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

Table 10. Multi-RAFT agents and RAFT polymerizations – Xanthate RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B]
'Z'-connected  **245*** PEO macro-RAFT agent	A[526,527]	VAc[526,527] *VAc*[526] VBz[527] VPv[527]
'R'-connected  **246**	A[528]	VAc[528]
 **247**	A*	VAc[502]

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

critical review of synthetic methods for RAFT agent synthesis which provides further details of the methods listed below.[28]

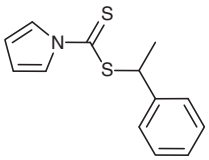
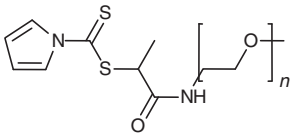
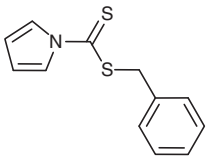
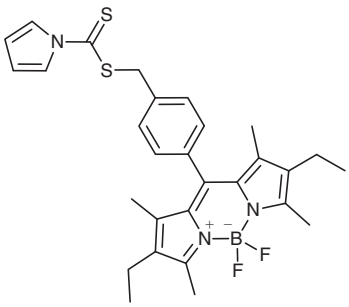
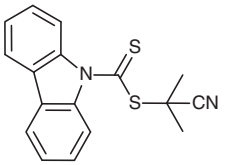
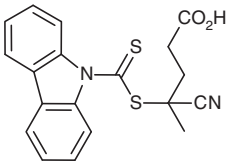
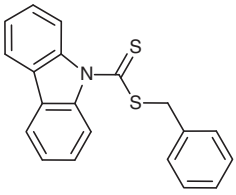
A. Reaction of a carbodithioate salt with an alkylating agent. O'Reilly and Hansell[474] have published on the synthesis of multifunctional trithiocarbonates The general conditions involve the use of acetone as solvent and phosphate as base as reported in a previous study from the same group.[552]
B. Reaction of a dithiochloroformate or a thiocarbonyl-bis-imidazole with nucleophiles. The esterification of a thiophenol with benzyl dithiochloroformate (e.g. Scheme 4) was used in the synthesis of a series of phenyl trithiocarbonates.[108] The dithiochloroformate may be replaced with the corresponding imidazolide to avoid use of thiophosgene (Scheme 5).[108]
C. Addition of a dithioacid across an olefinic double bond.
D. Radical-induced decomposition of a bis(thioacyl) disulfide.
E. Sulfuration of a thioloester or other substrate.
F. Radical-induced ester exchange.
G. Transesterification (thiol exchange by reaction of a dithioester with a thiol).
H. Base-catalyzed reaction of an activated halide (benzylic halide) with elemental sulfur.
I. Ketoform reaction (used for the synthesis of carboxy functional RAFT agents).

Many RAFT agents are derived indirectly by modification of other RAFT agents. Further description of those procedures used for the synthesis of macro-RAFT agents from polymers (and biopolymers) formed by non-RAFT processes appears in the section on block copolymers below.

J. Single monomer unit insertion. Chen et al.[433] have published further examples of the synthesis of RAFT agents (**150**, **151**) or macro-RAFT agents (**152**, see section on block copolymers below) by insertion of a single monomer unit into an existing RAFT agent. Houshyar et al.[109] examined the scope of RAFT single-unit monomer insertion for sequential insertion of St and NIPAm in detail. Critical factors for success were found to be a high transfer constant for the RAFT agent, such that only one monomer unit was added per activation cycle, and a high rate of addition of the radical ($R^{\bullet}$) to monomer relative to that for further propagation. Single unit monomer insertion can also be favoured over polymerization by use of equimolar amounts of monomer and RAFT agent. Zard and co-workers have reviewed[37] and reported further applications[492,553] of the use of single unit insertion of non-activated monomers into xanthates in organic synthesis. For example, insertion of *N*-vinylphthalimide provides a synthetic route to amines.[492]
K. Esterification or amidation (carbodiimide)
L. Esterification (acid chloride)
M. Esterification (Mitsunobu reaction)
N. Esterification (other)
O. Active ester-amine reaction or active ester-thiol reaction
P. 1,3-Dipolar cycloaddition
Q. Other methods

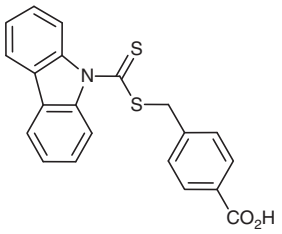
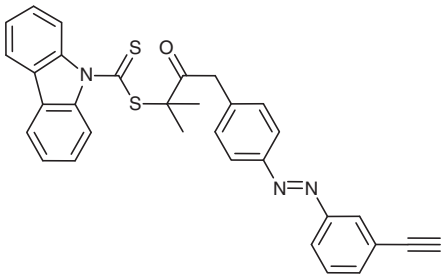
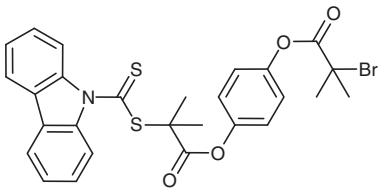
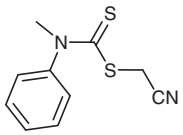
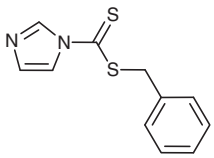
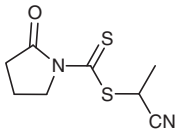
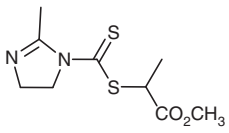
Examples of these processes are found in Tables 5–14 above.

Table 11. RAFT agents and RAFT polymerizations – Dithiocarbamate RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B]
 **248**	A*	St[114]
 **249** PEO macro-RAFT agent	A[533]	**360**/BAm[533]
 **250**	A*	MMA[534] MA[534] **364**[289] (NES)[290] (BES)[290] **452**[535] NIPAm/NVPI[517] MMA-*b*-PS[534] MA-*b*-PS[534] **364**-*b*-**387**[289]
 **251**	A[536]	NIPAm[536]
 **252**	D[537]	MMA[537]
 **253**	D[537]	MMA[537]
 **254**	A[134]	St[134]

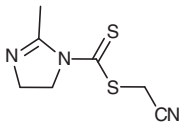
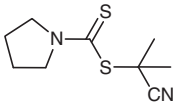
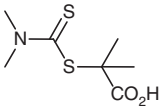
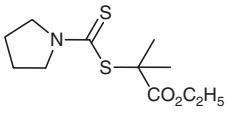
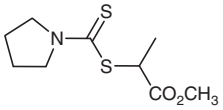
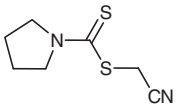
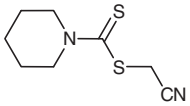
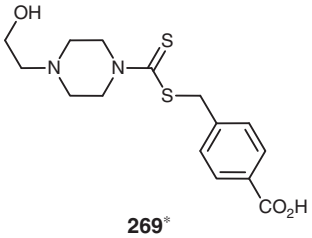
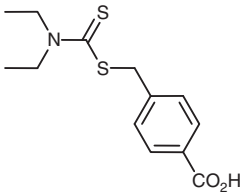
(*Continued*)

Table 11. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **255**	A	St[538] **388**[538]
 **256**	A[522]	St[522]
 **257**	A[539]	St[539] St-*b*-MA[539] St-*b*-AN[539] St-*b*-NIPAm[539]
 **258**	A*	VAc[366] VC[529]
 **259**	A*	**335**[540,541] **335**-*b*-St[541]
 **260**	–	(iPOx)[191]
 **261**	A[542]	(VAc)[542]

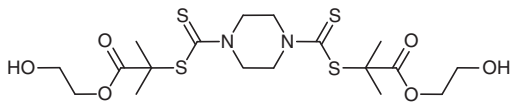
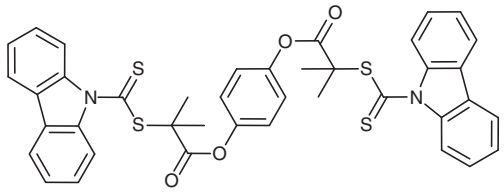
(*Continued*)

Table 11. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]
 **262**	A[542]	(VAc)[542]
 **263**	D[542]	(MMA)[542] (VAc)[542] (NVP)[542]
 **264**	H*	*BA/MAA/MMA/DAAm*[543]
 **265**	A[542]	(St)[542] (VAc)[542] (NVP)[542]
 **266**	A[542]	(VAc)[542] (NVP)[542]
 **267**	A[542]	(VAc)[542] (VBz)[542] (NVP)[542] (VAc-*b*-VBz)[542]
 **268**	A[542]	(VAc)[542]
 **269***	A[544]	**452**[535] **452**-*b*-St[535]
 **270**	A*[544]	**452**[535]

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

Table 12. Multi-RAFT agents and RAFT polymerizations – Dithiocarbamate RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B]
'Z'-connected  **271**	H*	(*BA*)[543] (*EA*)[543] (*EA/MMA/Am*)[543]
'R'-connected  **272**	A[539]	St[539] St-*b*-MA[539] St-*b*-AN[539] St-*b*-NIPAm[539]

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

Characterization of RAFT Agents and RAFT-Synthesized Polymers

Most papers on RAFT polymerization contain information on the characterization of RAFT agents, RAFT-synthesized polymers, and/or the RAFT process. In this section we consider papers where the characterization of RAFT agents and RAFT-synthesized polymers by spectroscopic or chromatographic methods is a primary focus.

The UV-visible spectra of an extensive series of an RAFT agents (ZC(=S)SR) have been examined.[554] The position of the absorbance maxima for the π–π* and n–π* transitions and the molar absorptivities were found to be dependent on both the 'Z' and 'R' substituents. Thus, changes in UV-visible spectra on conversion of an initial RAFT agent to a macro-RAFT agent need to be considered when using spectrophotometry to follow the course of RAFT polymerization. The crystal structure of the RAFT agent 2-[(dodecylsulfanyl)carbonothioylsulfanyl] propanoic acid (**155**) has been published.[555]

Two reviews contain significant reference to RAFT synthesized polymers.[556,557] The first details recent applications of mass spectrometry, in particular the matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) techniques, in polymer chemistry. The other is on application of multidimensional chromatography to polymers.[557] This typically involves some combination of high-performance liquid chromatography (HPLC) to separate a polymer sample according to composition and size-exclusion chromatography (SEC) or gel permeation chromatography (GPC) to separate according to molecular weight.[558]

Two dimensional HPLC/GPC methods have been applied to characterize poly(EHA)-*b*-poly(MA) formed by RAFT dispersion polymerization,[275] the block copolymers formed by hetero-Diels Alder coupling of RAFT-synthesized poly(iBoA) with ATRP-synthesized poly(MMA),[294] and the block and star-poly(St)-PCL formed by sequential RAFT and ring-opening polymerization.[319]

A combination of LC/MS and LC/FTIR was used to characterize poly(NVP) formed with an acid functional xanthate RAFT agent.[498] The rather poor control observed was attributed[498] to extensive chain transfer to dioxan (solvent). The likely acid-catalyzed degradation of the xanthate chain end was not mentioned.

Toxicity of RAFT-Synthesized Polymers

Many recent papers have explored the potential toxicity of RAFT-synthesized polymers. These polymers appear to be generally well tolerated in biological systems.

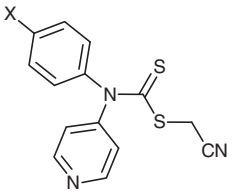
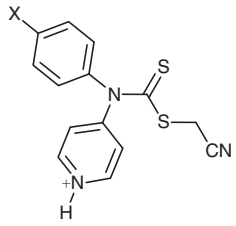
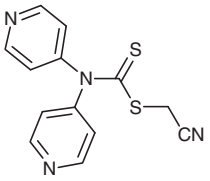
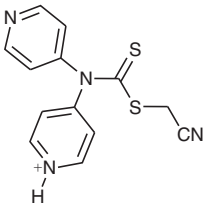
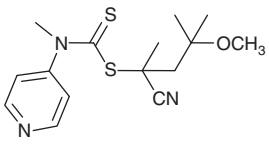
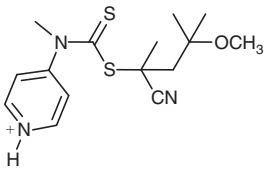
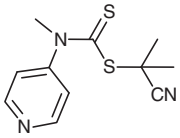
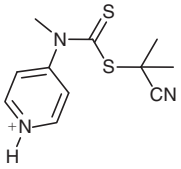
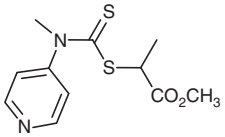
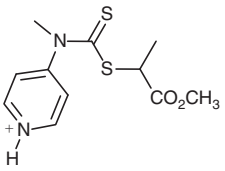
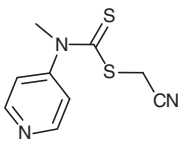
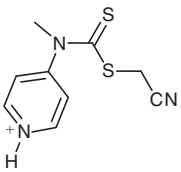
- Pissuwan et al.[559] found that, while poly(HPMAm)-dithiobenzoate showed some toxicity with three cell-lines when used at very high concentrations (1000 μM) but were well tolerated when used at lower concentrations (<200 μM), similar polymers with trithiocarbonate ends were non-toxic under all conditions.
- poly(DMAEMA)-*b*-poly(HEMA)-dithiobenzoate were shown to have low cytotoxicity with relation to block copolymers based on polyethyleneimine.[217]
- poly(DMAEA)-trithiocarbonate was shown to have low cytotoxicity and to degrade under physiological conditions to poly(AA).[444]

Polymerization Kinetics

Kinetic simulation is frequently used as a tool to correlate experimental data with theoretical models. The use of RAFT polymerization and kinetic simulation with Predici have been applied to determine chain length dependent termination rate constants in radical polymerizations using the RAFT-CLD-T method.[29] Kinetic simulation has also been used to study the mechanism of microwave-assisted RAFT polymerization of styrene (see below).[560] Kinetic simulation with a method of moments was used to model the effect of backmixing on the outcome of RAFT polymerization for a plug flow tubular reactor or for multiple continuous stirred tank reactors connected in series.[561]

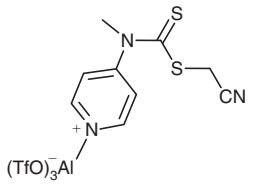
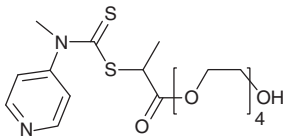
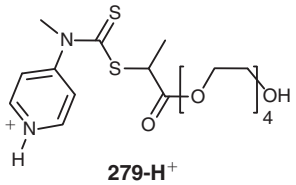
On-line monitoring of RAFT polymerization has been performed using ACOMP (automatic continuous online monitoring of polymerization reactions).[221,439,562] This technique

Table 13. RAFT agents and RAFT polymerizations – Switchable dithiocarbamate RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B]	RAFT agent	Polymerizations[B]
 **273a** X = OCH_3, **b** X = H, **c** X = F, **d** X = CN	A[115]	(MA)[115] NVC[115] VAc[115]	 **273a-H$^+$** X = OCH_3, **b-H$^+$** X = H, **c-H$^+$** X = F, **d-H$^+$** X = CN	MA[115]
 **274**	A[115]	(MA)[115] NVC[115] VAc[115]	 **274-H$^+$**	MA[115]
 **275**	D[531]	–	 **275-H$^+$**	MMA[531]
 **276**	D[531]	(VIm)[545]	 **276-H$^+$**	MMA[531] MMA-*b*-VAc[531]
 **277**	A*[531]	BA[531] NVC[531] NVP[531]	 **277-H$^+$**	DMAm[532] St[530,531] BA[531] (NVC)[531] St-*b*-MA[530,531] St-*b*-VAc[530,531] St-*b*-MA-*grad*-VAc[530,531]
 **278**	A*[531]	BA[531] VAc[531]	 **278-H$^+$**	DMAm[532] MA[531] DMAm-*b*-NVC[532] DMAm-*b*-NVP[532] DMAm-*b*-VAc[532]

(*Continued*)

Table 13. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B]	RAFT agent	Polymerizations[B]
–	–	–	 **278-Al(OTf)$_3$**	BA[531]
 **279**	A[532]	(DMAm)[532]	 **279-H$^+$**	DMAm[532]

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

involved passing a stream from the reaction mixture through a series of detectors including a multi-angle light scattering detector, a differential refractometer, a single capillary viscometer, and a photodiode array UV/visible spectrophotometer to provide on-line data on the variation of molecular weight and copolymer composition with polymerization time. The method has been applied to study the homopolymerization of BA in butyl acetate,[439] the copolymerization of BA with MMA,[562] and the copolymerization of DMAEMA with styrene in DMF[221] all with RAFT agent **155**.

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

The general guideline for choosing initiator concentrations for RAFT polymerization is that the mole ratio of RAFT agent to amount of initiator decomposed should be $>10:1$ and be such that the molar mass obtained in a control experiment (i.e. same conditions without RAFT agent) is at least 10-fold higher than the desired molar mass.[17] It must be remembered that for every pair of radicals generated, a pair of radicals will terminate to provide dead polymer impurity.

In some cases, it may be necessary to use a higher than desirable initiator concentration to achieve a more acceptable rate of polymerization. Before taking this step, avoidable causes of retardation need to be considered. These causes include: inappropriate choice of RAFT agent, impurities in the RAFT agent (or other components of the polymerization medium), and ineffective exclusion of air or oxygen.

RAFT polymerizations have been successfully conducted at temperatures ranging from sub-ambient to 140°C (or higher under very high pressure). At lower temperature, transfer constants may be lower and retardation may become more important. At higher temperatures, the RAFT agent may be unstable. The importance of these phenomena depends on the specific RAFT agent and monomer combination.

ATRP-Initiated RAFT Polymerization

Several studies have appeared on the use of initiators normally associated with ATRP (halide or sulfonyl halide plus transition metal catalyst) to initiate RAFT polymerization. The process may use a variety of traditional ATRP or SET-RDRP and have been called SET-RAFT.[346,384] Examples include:

- the use of a metalloenzyme (laccase) as an catalyst and ethyl bromoisobutyrate as initiator to perform RAFT polymerization of PEGMA in the presence of cyanoisopropyl dithiobenzoate (**12**).[185]
- polymerization of MA with cyclic RAFT agent **444** and either ethyl 2-bromopropionate or 2-diethyl, meso-2,5-dibromoadipate as initiator and CuBr/tris[(2-pyridyl) methyl]amine catalyst.[563]

RAFT Agent Stability During RAFT Polymerization

Li et al.[221] have reported that some trithiocarbonate RAFT agents (**18**, **89**, **155**) are unstable during polymerization of DMAEA at 80°C in DMF. The RAFT agents were stable during BA and St polymerization under similar conditions and a lower rate of degradation was observed in the case of DMAEA/St copolymerizations. The result is surprising since many other groups have reported no specific difficulties in RAFT polymerization of this or other monomers with tertiary amine functionality.

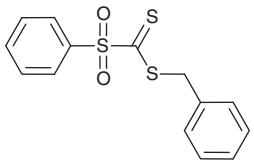
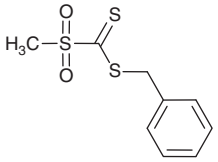
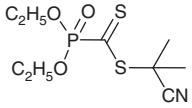
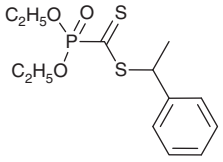
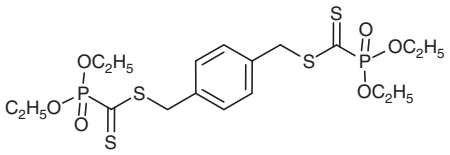
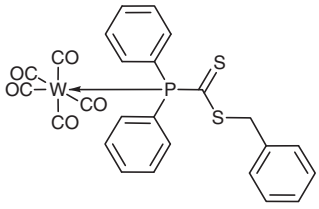
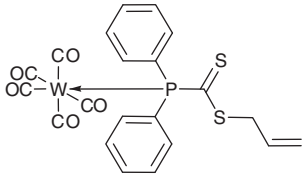
Oxidation of the RAFT agent/end-group was proposed to account for loss of living character during RAFT polymerization of St with 1-phenylethyl dithiobenzoate in air.[162]

RAFT polymerization is not usually compatible with unprotected primary or secondary amines. Janoschka et al.[209] have reported that RAFT polymerization can be successfully carried out in the presence of an unprotected hindered amine (2,2,6,6-tertramethylpiperidene) functionality in the methacrylate **194**. However, the polymerization had to be conducted in aqueous ethanol as solvent (polymerization was not successful in toluene) and with a higher than usual concentration of initiator.

Microwave-Assisted RAFT Polymerization

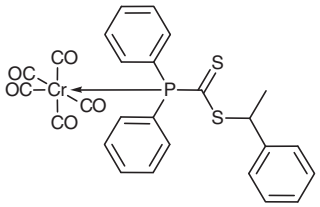
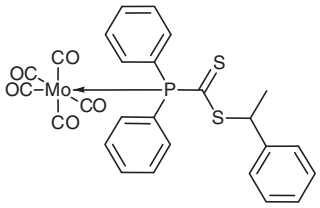
Three reviews on microwave-assisted polymerization[65,98,99] and two reviews specifically on microwave-assisted RAFT polymerization[30,31] have appeared. The number of papers on

Table 14. RAFT agents and RAFT polymerizations – Other RAFT agents

RAFT agent	Synthesis[A]	Polymerizations[B,C]
 **280**	B[546]	(BA)[546] (MA)[546] (tBA)[546] (MMA)[546] iBoA[546,547]
 **281**	B[546]	–
 **282**	*	HEA[297]
 **283**	*	–[C]
 **284**	**A**[548]	–[C]
 **285**	A[286]	St[286] BA[286]
 **286**	A[286]	BA[286]

(*Continued*)

Table 14. (Continued)

RAFT agent	Synthesis[A]	Polymerizations[B,C]
 **287**	A[549]	St[549] BA[549] St-*b*-BA[549]
 **288**	A[549]	St[549] BA[549]

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

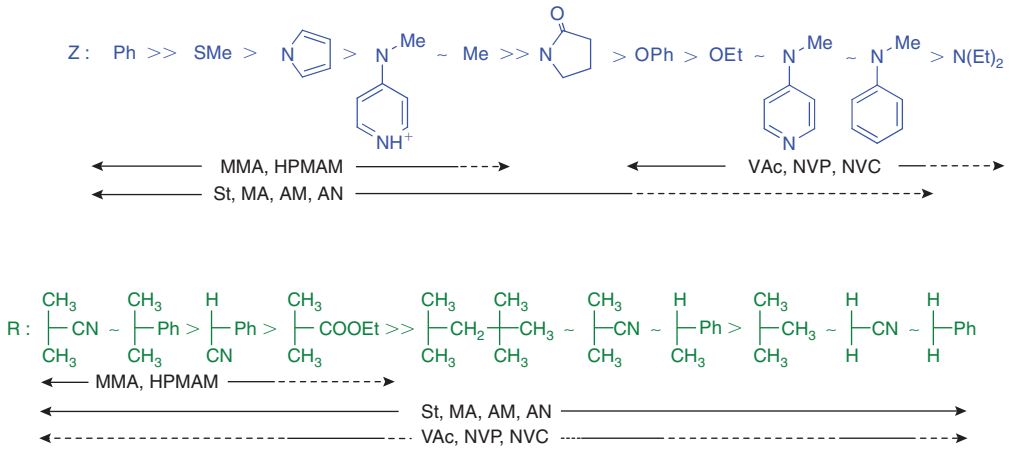


Fig. 4. Guidelines for selection of RAFT agents for various polymerizations.[17–19,137,550] For Z, addition rates decrease and fragmentation rates increase from left to right. For R, fragmentation rates decrease from left to right. Dashed line indicates partial control (i.e. control of molar mass but poor control over dispersity or substantial retardation in the case of VAc, NVC, or NVP).

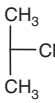
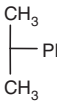
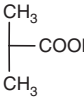
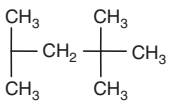
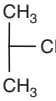
RAFT polymerizations accelerated by microwave heating continues to increase. Recent examples include RAFT polymerization of MMA,[564] acrylamides (NIPAm, DMAm) and their block copolymers,[392] vinylsilazane (**452**),[535] and vinyl esters (VAc, VBz, VPv) and their block copolymers.[523] Each of these studies indicate substantial acceleration of polymerization with respect to similar conventionally heated polymerizations.

Controversy over the extent and mechanism of acceleration of the rate of RAFT polymerization continues. Two groups[560,565] have reported on kinetic-modelling of microwave accelerated RAFT polymerization of St in an attempt to gain further understanding of the process. Both came to the conclusion that there is a 'microwave effect'. The first study[560] attributed accelerated polymerization to an additional initiation process. The second study[565] discounted this possibility and proposed that the results were consistent with the rate constants for addition to monomer (k_p) and RAFT agent (k_{add}) both being accelerated to the same extent by microwave irradiation.

In two independent studies[366,391] of accelerated RAFT polymerization in conventionally heated continuous-flow tubular reactors (see below), microwave-heated batch RAFT polymerizations were conducted as control experiments. No significant differences in polymerization kinetics were observed. These results suggest there is no 'microwave effect' beyond that of rapid heating of the reaction medium.

In their perspective, Kempe et al.[99] conclude with reference to apparent 'microwave effects' that 'most of the differences seem to be ascribable to the application of different equipment' and that 'these differences might be due to a non-exact control and measurement of the temperature and inhomogeneous electric fields'. In the absence of other data, we concur with this conclusion.

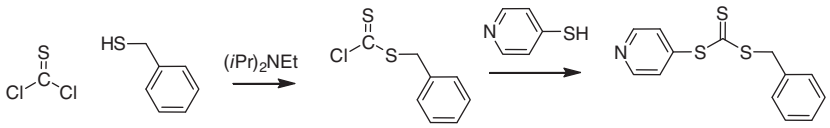
Table 15. Guidelines for the selection of RAFT agents[A,B,C,D]

Class	Aryl dithioester	Trithiocarbonate	Alkyl or aralkyl dithioester	Aromatic dithiocarbamate	Lactam dithiocarbamate	O-aryl xanthate	O-alkyl xanthate	N-alkyl–N-aryl dithiocarbamate	N,N-dialkyl dithiocarbamate
R \ Z	Ph	SCH_3	CH_3			OPh	OCH_3	$NPh(CH_3)$	$N(CH_3)_2$
	**MMA** **St** **MA** VAc	**MMA** **St** **MA** VAc	MMA **St** **MA** VAc	**MMA** **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA **VAc**	MMA St MA **VAc**	MMA St MA VAc
	**MMA** **St** MA VAc	**MMA** **St** **MA** VAc	MMA **St** **MA** VAc	**MMA** **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc
	**MMA** **St** **MA** VAc	**MMA** **St** **MA** VAc	**MMA** **St** **MA** VAc	**MMA** **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc
	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA VAc	MMA St MA **VAc**	MMA St MA **VAc**	MMA St MA VAc
	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc
	MMA **St** MA VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA **VAc**	MMA St MA **VAc**	MMA St MA VAc
	MMA **St** MA VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc
	MMA **St** MA VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc
	MMA **St** MA VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA **VAc**	MMA St MA **VAc**	MMA St MA VAc
	MMA **St** MA VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA **St** **MA** VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc
	MMA **St** MA VAc	MMA **St** **MA** VAc	MMA **St** MA VAc	MMA **St** MA VAc	MMA **St** MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc
	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc	MMA St MA VAc

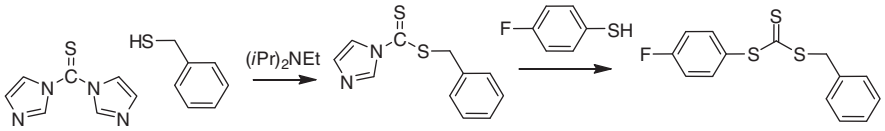
[A] **Bold** = controls well; regular = controls, but not so well; grey = does not control.
[B] The activity of the switchable RAFT agents (Table 13) is similar to that of *N*-alkyl-*N*-aryl dithiocarbamates in unswitched state and similar to that of the aromatic dithiocarbamates in their switched or protonated state.
[C] See the section *Abbreviations* for definitions of the monomer abbreviations.
[D] Table adapted from Ref. [551], copyright John Wiley and Sons.

RAFT in Continuous Flow

Solution RAFT polymerization of MMA, BA, VAc, NIPAm, and DMAm has been performed in tubular reactors.[366,391] It was important to degass the polymerization medium and to use metal (stainless steel) tubing for the process.[366] Under these conditions low dispersity polymer similar to those obtained in batch (microwave heated) experiments were obtained. Oxygen-induced inhibition was observed with the use of standard PFA



Scheme 4. Synthesis of aryl benzyl trithiocarbonate using thiophosgene.



Scheme 5. Synthesis of aryl benzyl trithiocarbonate using 1,1′-thiocarbonyldiimidazole.

tubing.[366] A procedure for sequential RAFT polymerization and end-group removal in a single flow process has also been reported.[566]

Models have been developed to describe RAFT polymerization in tubular reactors or a series of continuous stirred tank reactors (CSTRs) or a combination of these. Kinetic simulation was then used to predict residence time distributions and the effect of backmixing on the outcome of the process.[561,567] The effect of backmixing is to produce a higher dispersity and a lower average chain length than that expected based on reagent concentrations and conversion, thus it becomes important to exclude reactor backmixing as much as is possible.[561] Methods have also been developed to allow prediction of the monomer sequence distribution for such reactors.[567]

A droplet microfluidic reactor has been described and used to prepared low dispersity poly(St)-*b*-poly(MMA).[534]

RAFT Polymerization in Ionic Liquids

Ionic liquids have been reported to significantly enhance both the reaction rate and polymer molecular weight in radical polymerization. These effects have been attributed to a reduction in the termination rate constant. Barth et al.[29] have used SP-PLP-EPR measurements to determine termination rate constants (k_t) for MMA-d_8 polymerization in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF4) and 1-ethyl-3-methylimidazolium bis(tri-fluoromethylsulfonyl) imide ([emim]NTf2). Both the average $<k_t>$ and the value of $k_t^{1,1}$ for reaction between single unit chains were significantly reduced with respect to values for bulk MMA.

Control of Stereochemistry in RAFT Polymerization

Smith et al.[521] observed a higher than usual tacticity (probability of a racemo dyad $r = 100 \times [rr + mr/2]/[rr + mr + rr] = 69 \pm 8\,\%$) for a low molar mass ($M_n$ 1000) poly(VAc) prepared by RAFT polymerization with xanthate **235** at 50°C. A value of r of 53 % was obtained for higher molar mass ($M_n > 1300$) poly(VAc) for temperatures in the range 37–60°C.

The tacticity of low molar mass NIPAm (M_n 4000) prepared with trithiocarbonate (**79**) was found to be significantly more syndiotactic ($r = 58.6\,\%$) than NIPAm produced by conventional radical polymerizations (without RAFT agent $r = 54.6\,\%$).[321] This was attributed to an effect of the acid functional end-group. The syndiotacticity was further enhanced ($r = 61.1\,\%$) for polymerization with 3-methyl-3-pentanol as cosolvent.

In order explore the effects of molecular weight and tacticity on the glass transition temperature, Biswas et al.[316] prepared poly(NIPAm) (M_n in the range 70000–100000) with differing tacticity by RAFT polymerization with dithioester **73** in the presence of yttrium triflate ($Y(OTf)_3$) at 60°C. r was in the range 53 % (no $Y(OTf)_3$) to 12 % (0.266 M $Y(OTf)_3$). Katsumoto et al.[284] prepared poly(DEAm)s with differing tacticity by RAFT polymerization in the presence of $Y(OTf)_3$ or $Sc(OTf)_3$.

A high syndiotacticity was obtained in RAFT polymerization of the donor–acceptor–donor monomer, *N*-(6-acetamidopyridin-2-yl)acrylamide (**359**), with either **11** or **93** in the presence of 1-octylthymine at 60°C.[170] The value of r was raised from 44 %, for no 1-octylthymine, to 73 %, with 2 molar equivalents of 1-octylthymine with respect to monomer.

A process for forming stereogradient poly(MMA) has been described.[173] The process involves RAFT copolymerization of MAA with a bulky methacrylate such as TPMMA or 1-phenyldibenzosuberyl methacrylate (**293**) with **11** in toluene solution. Under these conditions, MAA showed increased reactivity, attributed to hydrogen bonding, and was consumed slightly faster than either TPMMA or **293**. The copolymers were converted into homo-poly(MAA) by the acid hydrolysis and then to homo-poly(MMA) by esterification with trimethylsilyldiazomethane. The fraction of isotactic triads in the poly (MAA) changed gradually from $mm = 14\,\%$ to nearly 100 %. RAFT copolymerization of TPMMA and MAA in 1,4-dioxane resulted in consumption of MAA and the bulky methacrylate at the same rate and an atactic polymer ($rr/mr/mm = 38/49/13$).

RAFT Polymerization in Heterogeneous Media

Several reviews that relate to the use of RAFT in heterogeneous media have appeared[32,96,97] including a tutorial review on RAFT in microemulsion.[32] Examples of RAFT polymerizations in heterogeneous media are included in Tables 3–14 and are distinguished in the tables by the monomer appearing in italics.

Ab initio RAFT emulsion polymerization has been plagued by problems of retardation, colloidal instability, poorly defined molecular weight distributions and broad, possibly multimodal, particle size distributions. Success was strongly dependent on the specific RAFT agent and the monomers polymerized. This is attributed in part to the slow transportation of the RAFT agent between the droplet phase and the particle phase and in part to the way in which molecular weight distributions evolve during RAFT polymerization. Those RAFT experiments in heterogeneous polymerization that were successful were mostly multistep processes, used amphiphilic macro-RAFT agents, and/or made use of miniemulsion or seeded emulsion techniques.

The use of amphiphilic macro-RAFT agents as stabilizers in ‘surfactantless’ polymerization by emulsion, miniemulsion,

dispersion and other methods continues to attract attention. Recent examples include:

- One pot RAFT dispersion polymerization to form PEO-*b*-poly(St) vesicles in methanol using PEO-macro-RAFT agent **132**,[410] and form poly(GMA)-*b*-poly(HPMA) in water using a poly(GMA) macro-RAFT agent (GMA units are present as 2,3-dihydroxypropyl methacrylate units).[186]
- Sequential formation of PEGA/MMA macro-RAFT agent (by solution polymerization) and low dispersity poly(PEGA-*co*-MMA)-*b*-poly(St) (by emulsion polymerization) in a one-pot process.[354,360] The same macro-RAFT agent was also used in non-aqueous emulsion or dispersion polymerization of BzMA.[361]
- Hollow nanoparticles were prepared by miniemulsion polymerization of MMA with DVB crosslinker using a MAA/MMA macro-RAFT agent.[368]
- Shell-crosslinked fluorinated nanocapsules were prepared by miniemulsion polymerization of HA/DFHA with DVB crosslinker using a MAA/DFHA macro-RAFT agent.[369]
- Emulsion polymerization of VAc was performed with a xanthate-terminated dextran as RAFT agent.[568]
- Gradient copolymers of TFEMA and AA were synthesized using an amphiphilic RAFT agent and starved feed addition of TFEMA.[438]
- Emulsion or dispersion polymerization was carried out in supercritical CO_2 of VAc with a PEO macro-RAFT agent (**245**),[526] of MMA with a PDMS macro-RAFT (**148**),[431] or of NVP with VAc/VPv[513] macro-RAFT agents agent as stabilizer.
- See also the section below on *Microgels and Nanoparticles* and Table 24 for examples of RAFT crosslinking polymerization.

RAFT miniemulsion polymerization of St was performed in supercritical CO_2 at 50°C with trithiocarbonate **175**, an aqueous phase initiator (VA-044), and the anionic surfactant Dowfax 8390.[458] It was found that the particle size could be tuned by changing the CO_2 pressure while keeping the recipe constant, with 6.00, 6.50, and 7.50 MPa, generating number-average particle diameters of 98, 89, and 48 nm, respectively.

It has also been found that, particularly in *ab initio* processes, improved control and colloidal stability is obtained for monomer RAFT agent combinations which have a lower transfer constant. In this context several groups have studied the kinetics of the RAFT emulsion polymerization of St[495,510] with xanthate RAFT agents. A detailed study of RAFT microemulsion of BA with xanthate RAFT agents has also been performed.[32,500,501] It was found that a simplified RAFT mechanism ($k_{add} = k_{tr}$, no intermediate radical termination) allowed the kinetics of the microemulsion polymerization of BA with a xanthate RAFT agent to be quantitatively predicted.[32,500] With this model, the value of k_β was found to be important in determining the monomer conversion. Another study used kinetic simulations of a RAFT microemulsion polymerization to show that retardation and inhibition can be explained through consideration of the exit and re-entry of the $R^\bullet$ radicals without invoking 'slow fragmentation' or 'intermediate radical termination' phenomena.[569] Note, however, that the finding that data can bit fit by a simple model does not prove that model.

RAFT polymerization of DMAm in inverse microemulsion has been described.[326,570] The process has been performed with a series of trithiocarbonate RAFT agents.[326] The relative efficacy of these was attributed to the partition coefficient between the aqueous and oil phase.

Polymer self-assembly may be considered an integral part of the initial phase of heterogeneous polymerization and it is well known that amphiphilic polymers of various architectures undergo spontaneous self-assembly in aqueous solution to provide a wide range of nanostructures, which include spherical, worm-like and rod-like micelles, vesicles, nanotubes, and toroids. Nonetheless, the (RAFT) polymerization induced self-assembly and the factors which control what structure is formed have recently attracted considerable interest with studies on the phenomenon in emulsion polymerization,[354,381,400] dispersion polymerization[187,224,229,353,361,571] and non-aqueous dispersion polymerization.[394,397] Blanazs et al.[187] have constructed a phase diagram for poly(**288**)–poly(HPMA). Refer also to Table 24 for examples of the synthesis of microgels and core-crosslinked star polymers by RAFT-mediated radical crosslinking polymerization most of which can be considered as dispersion polymerizations.

RAFT Polymer Syntheses

Polymer syntheses by RAFT polymerization are summarized in Tables 3–14. Only systems which require separate comment are mentioned here or in the subsequent sections. Some of the more exotic monomers subjected to RAFT polymerization are included in the tables that follow. They include methacrylates (Fig. 5), acrylates (Fig. 6), methacrylamides (Fig. 7), acrylamides (Fig. 8), styrene derivatives (Fig. 9), and vinyl monomers (Fig. 10). Monomers of the above classes with reactive functionality appear in Figs 11 and 12. There continues to be substantial interest in RAFT polymerization of various biorelated monomers which include those derived from amino acids,[572] such as acrylamides **363**–**368** (Fig. 8), St derivative (**384**), and glycomonomers, such as methacrylates **312**, **313**, and **318**–**320** (Fig. 5), acrylates **341** and **351**, methacrylamides **352**–**355**, acrylamide **372**, and St derivative **393**. Note that such polymers are frequently also made by modification of polymers with reactive post-RAFT polymerization (e.g. those formed from monomers with active ester groups, Fig. 12).

Methacrylates

A wide range of methacrylates have been successfully polymerized, which include AAEMA, AEMA, AMA, CMA, BMA, BDSMA, DEGMA, DMAEMA, EGMA, HEMA, HMA, iBMA, LMA, MMA, MPC, PEGMA, PFPMA, TMAEMA, TMAPMA, TPMMA (see *Abbreviations*), (**289**–**333**) given in Fig. 5, and compounds **400**, **407**, **413**, and **430**. Low dispersities in RAFT polymerization of methacrylates require the use of a RAFT agent with a high transfer constant. This requires that the 'Z' group is suitable for MAMs and that the 'R' group is a good leaving group with respect to the methacrylate propagating radical. Suitable RAFT agents include dithiobenzoates, **11**, **12**, **18**, and **40**, trithiocarbonates, **95** and **98**, and aromatic or switchable dithiocarbamates in their more active form, **275-H$^+$** and **276-H$^+$**, and derivatives of these.

The polymers poly(NVC)-*b*-poly(**311**) and poly(NVC)-*b*-poly(**314**) were apparently prepared making use of a poly (NVC) macro-RAFT agent with xanthate RAFT agent **221** and, for the case of poly(NVC)-*b*-poly(**314**), good control (a low dispersity polymer) was reported.[496] However, *O*-alkyl xanthate RAFT agents do not normally provide good control over the polymerization of methacrylates.[573] Furthermore, the

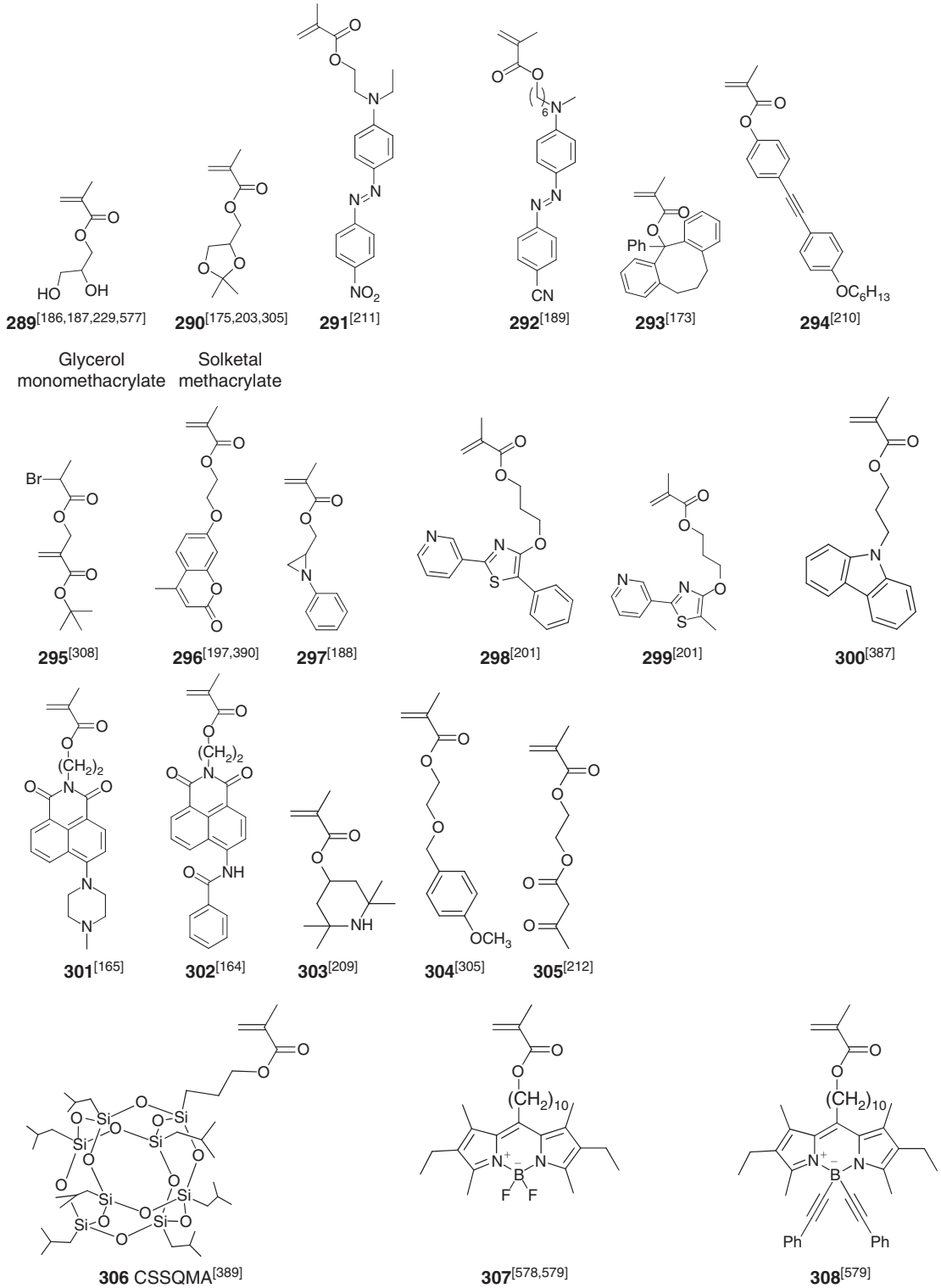


Fig. 5. Methacrylate monomers (**289**–**333**) subjected to RAFT polymerization.

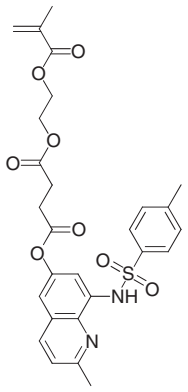
poly(NVC) propagating radical is anticipated to be a poor leaving group with respect to the propagating species formed from either **311** or **314**.

Monomer **329** containing a xanthate functionality is included in Fig. 6 because with 'R' = primary alkyl that functionality does not function as a RAFT agent. It was used as a precursor to a polythiol.

Acrylates

Acrylates mentioned in this survey include AEP, BA, CPA, DA, DEHEA, DMAEA, EA, EAA, EEA, EHA, iBoA, MA, PA, PEGA, tBA, and (**334**–**351**) listed in Fig. 6.

Acrylate esters undergo chain transfer to polymer during polymerization leading to branched and even gelled polymers. It has been reported that the extent of branching is higher



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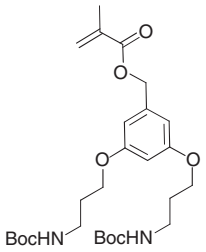

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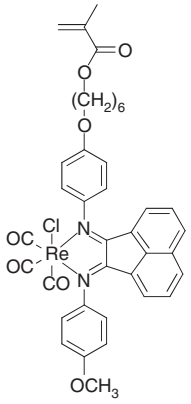

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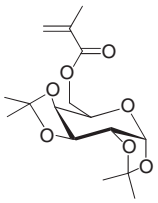
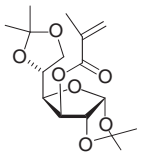
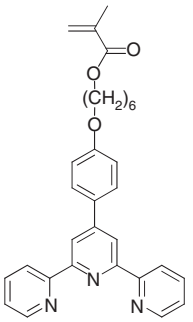


312[166]



313[216,230]



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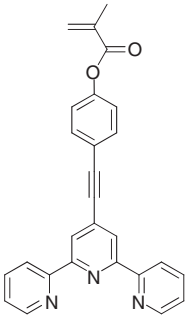

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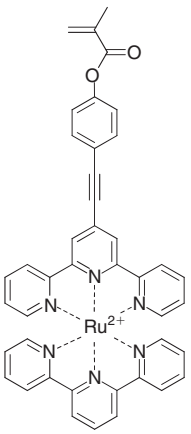

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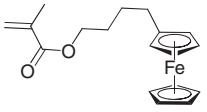


317[311]

Fig. 5. (*Continued*)

for conventional radical polymerization than for RDRP (ATRP, RAFT, and NMP).[443] A qualitative explanation was proposed in terms of the differences in the concentrations of short-chain radicals between RDRP and conventional radical polymerization. Reys and Asua[574] have proposed an alternative explanation in terms of radical life times (the time between chain activation and deactivation) being of the same order of magnitude or shorter than the time required for the conformation change necessary for intramolecular hydrogen atom transfer. A recent paper suggests that conventional chain transfer agents (*n*-octanethiol)[575] and H-bonding solvents (*n*-butanol)[576] also reduce the extent of branching in conventional radical polymerization.

Methacrylamides

Many examples are appearing of RAFT (co)polymerization of HPMAm; particularly with respect to various bioapplications.[54] Other examples of methacrylamides monomers recently used in RAFT polymerization are the primary amino-functional monomers, AEMAm and APMAm, DEAPMAm, DMAPMAm, **409** and (**352**–**358**) shown in Fig. 7. The choice of RAFT agent for polymerization of methacrylamides is subject to similar constraints as mentioned for the methacrylates. In particular the 'R' group should be selected so as to be a good leaving group with respect to the propagating radical. The RAFT agents generally preferred include dithiobenzoate **18** and ethyl trithiocarbonate **97** and derivatives of these.

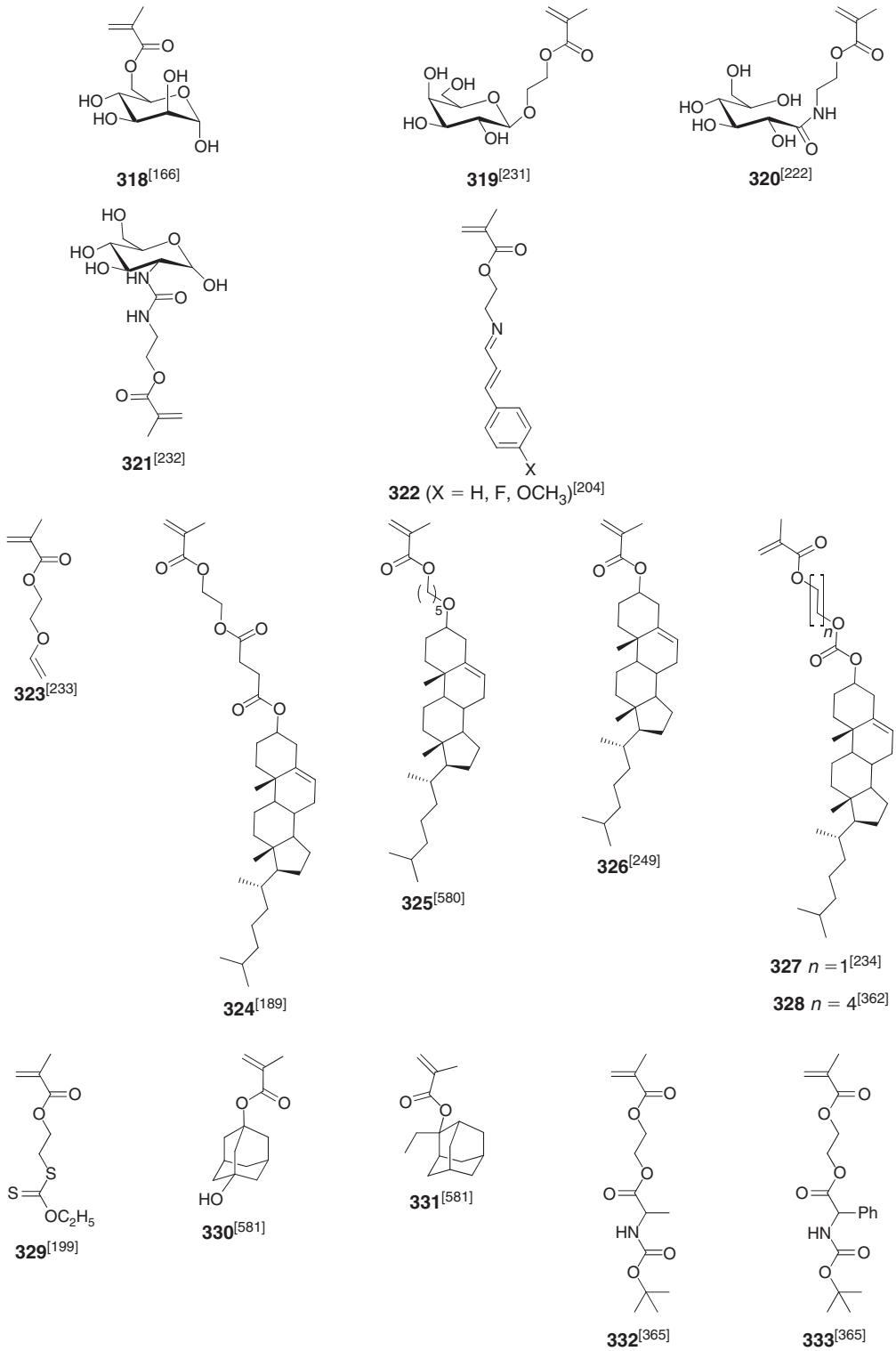


Fig. 5. (*Continued*)

Acrylamides

Attaining low dispersities with RAFT polymerization of acrylamides requires a RAFT agent suitable for MAMs. Acrylamides include Am, AMPS, BzAm, CHAm, DAAm, DEAm, DMAm, DMAEAm, NIPAm, NAM, OAm (see *Abbreviations*) and (**359**–**372**) shown in Fig. 8.

Styrenics

Styrenic monomers subjected to RAFT polymerization include (**373**–**393**) in Fig. 9 plus **399**, **404**, **405**, and **406**. Good control over RAFT polymerization of St and derivatives requires a RAFT agent suitable for MAMs. Many of the functional styrenes in Fig. 9 have been used to prepare polymers for optoelectronic

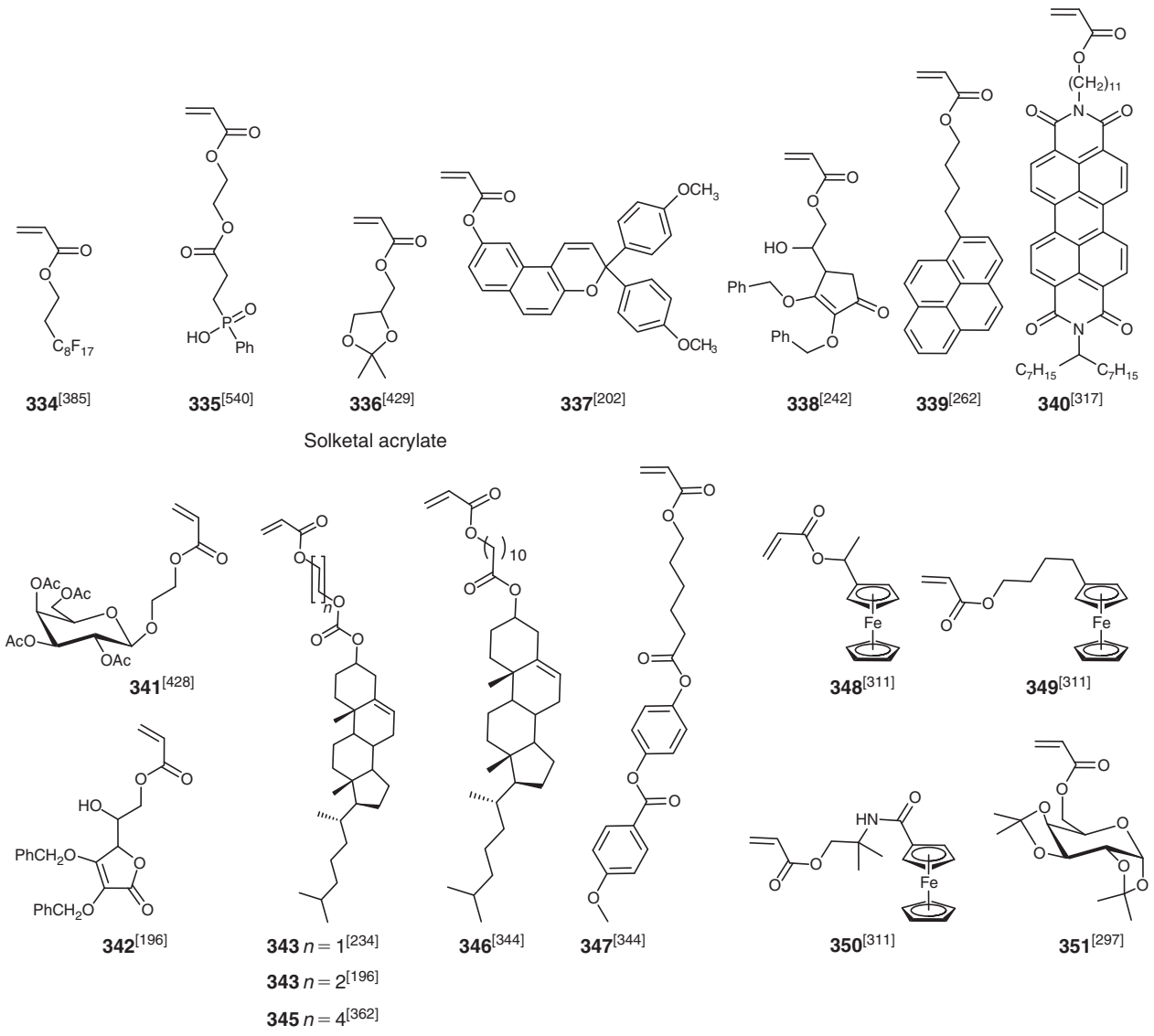
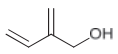


Fig. 6. Acrylate monomers (**334**–**351**) subjected to RAFT polymerization.



394[396]

Chart 3.

applications. The advantage of the styrenic monomers in this context is that the functionality is typically not attached through a potentially labile ester or amide linkage.

Diene Monomers

RAFT polymerization of diene monomers generally requires a more active RAFT agent and generally requires use of higher reaction temperatures to obtain good control and reasonable rate of polymerization (e.g. 125°C). RAFT homopolymerizations of BD and Ip in solution are slow.[437] The RAFT copolymerization of Ip with hydroxy-functional monomers, HEMA, HEA, and **394** (Chart 3), with trithiocarbonate (**123**) has been explored.[396] Diels Alder reaction of Ip with the (meth)acrylates was observed as a side reaction. The (meth) acrylates are consumed preferentially to Ip. thus their copolymers with Ip have a gradient structure. The copolymer of Ip with **394** had a more random structure.

Vinyl Monomers

Vinyl monomers in the present context include the vinyl esters (VAc, VB, VBz), the *N*-vinyl amides and imides (NVCL, NVPip, NVP, NVPI), the *N*-vinyl heteroaromatics (Vim, NVC), vinylsulfonates (BES, NES), vinylphosphonic acid (VPA), the haloolefins (VF2), and others in Fig. 10. Most of these monomers are LAMs (except **395**) and good control over homopolymerization requires use of a RAFT agent suited for that class of monomer (usually a xanthate or a dithiocarbamate). Note, however, that good control over copolymerization of LAMs with MAMs can be obtained with RAFT agents suited to MAMs (e.g. NVPI/NIPAm with **251**[517]).

The polymerization of NVP in aqueous media was reported as problematic due to the sensitivity of the macro-RAFT agent with a terminal NVP unit to hydrolysis. It has recently been shown[506,507] that this problem can be overcome by conducting the polymerization at ambient temperature with redox initiation.

A study on the use of benzyl and *t*-butyl trithiocarbonate and dithiobenzoate RAFT agents for VAc polymerization has

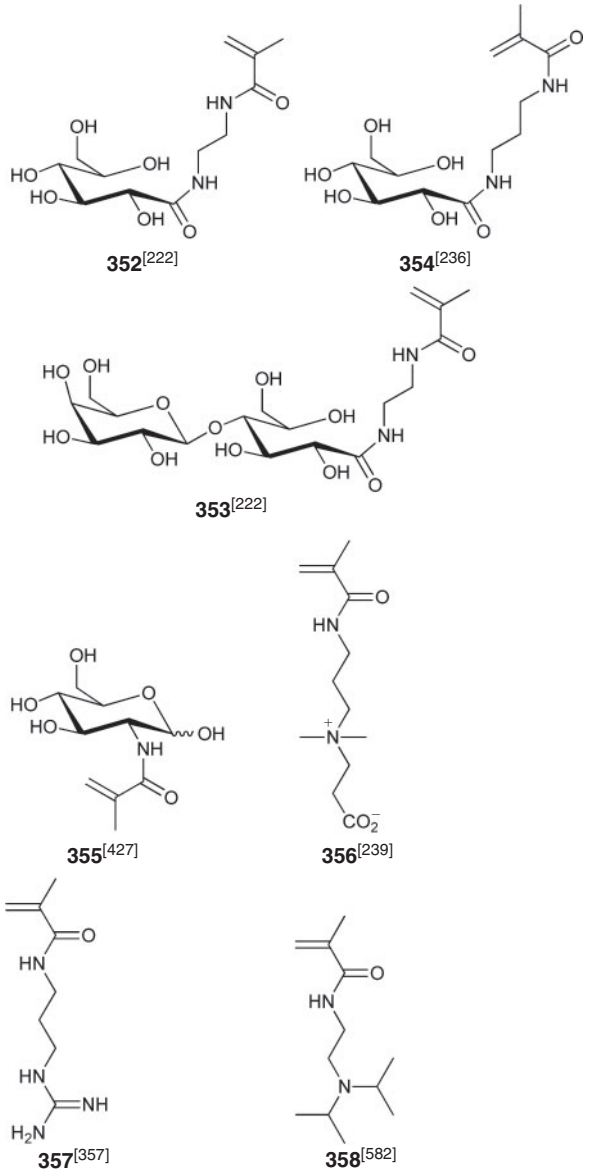


Fig. 7. Methacrylamide derivatives (**352**–**358**) subjected to RAFT polymerization.

appeared.[274] Intermediate radical termination was found to be a significant cause of retardation with these systems.

Monomers with Reactive Functionality

There is a need for processes for polymer modification post-RAFT polymerization (so-called polymer analogous reactions) that proceed in quantitative yield under mild reaction conditions. Several reviews on combined use of RDRP and 'click chemistry' have appeared.[66–72] The 'clickable' functionality may be present on the Z or R groups of the RAFT agent (see elsewhere in this review) or in the monomers. These monomers can be incorporated in blocks as a precursor to a polymer brush or copolymerized to provide sites for the attachment of functionality or for crosslinking. Many papers concern the combination of RAFT and azide-alkyne 1,3-dipolar cycloaddition. Some alkyne-functional monomers are listed in Fig. 11. Azide functionality is often incorporated post RAFT polymerization.

'Active ester' monomers that have been subject to RAFT polymerization (**401**–**405**) are shown in Fig. 12. These active

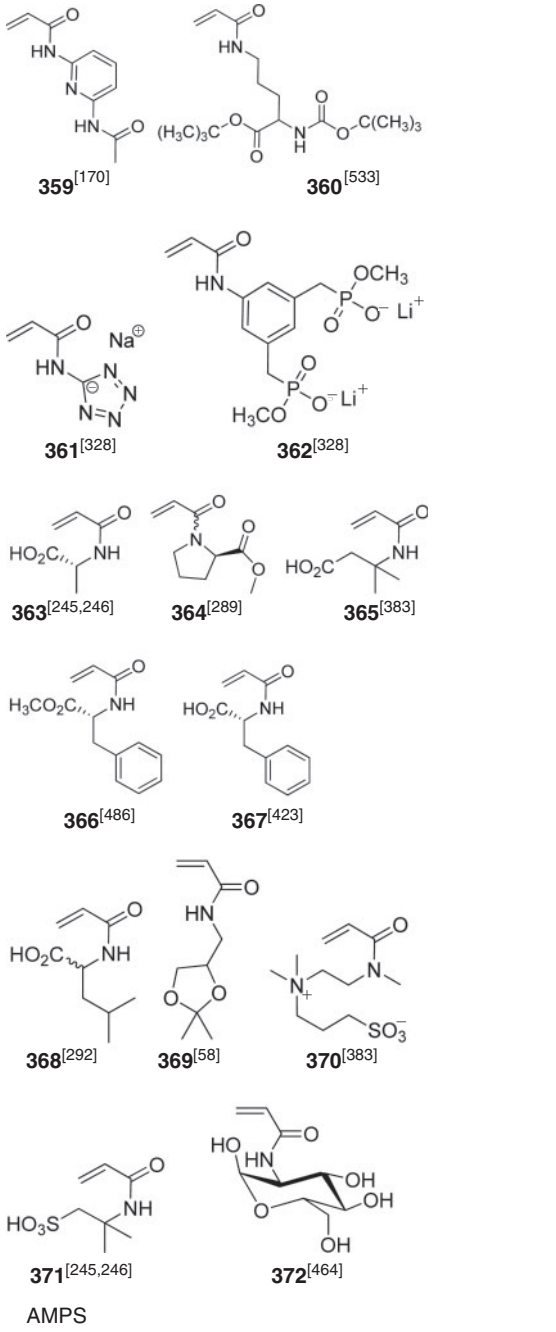


Fig. 8. Acrylamide derivatives (**359**–**372**) subjected to RAFT polymerization.

ester groups undergo facile reaction with, in particular, substrates with primary amine functionality. Monomers with protected thiol, hydrazide or amino functionality that have been subjected to RAFT (co)polymerization are shown in Fig. 13.

Several recent papers have explored polymerization of monomers containing isocyanate or isothiocyanate functionality (Fig. 14).[192,243,288] RAFT polymerization and the thiocarbonylthio group is compatible with isocyanate functionality. However, some care must be taken in selection of the RAFT agent and other components of the polymerization medium such that they do not also contain other functionality that is inherently reactive (such as carboxy).[243]

Monomers **416** and **417** with ATRP initiator functionality include CMS and the monomers shown in Fig. 15.[203,587]

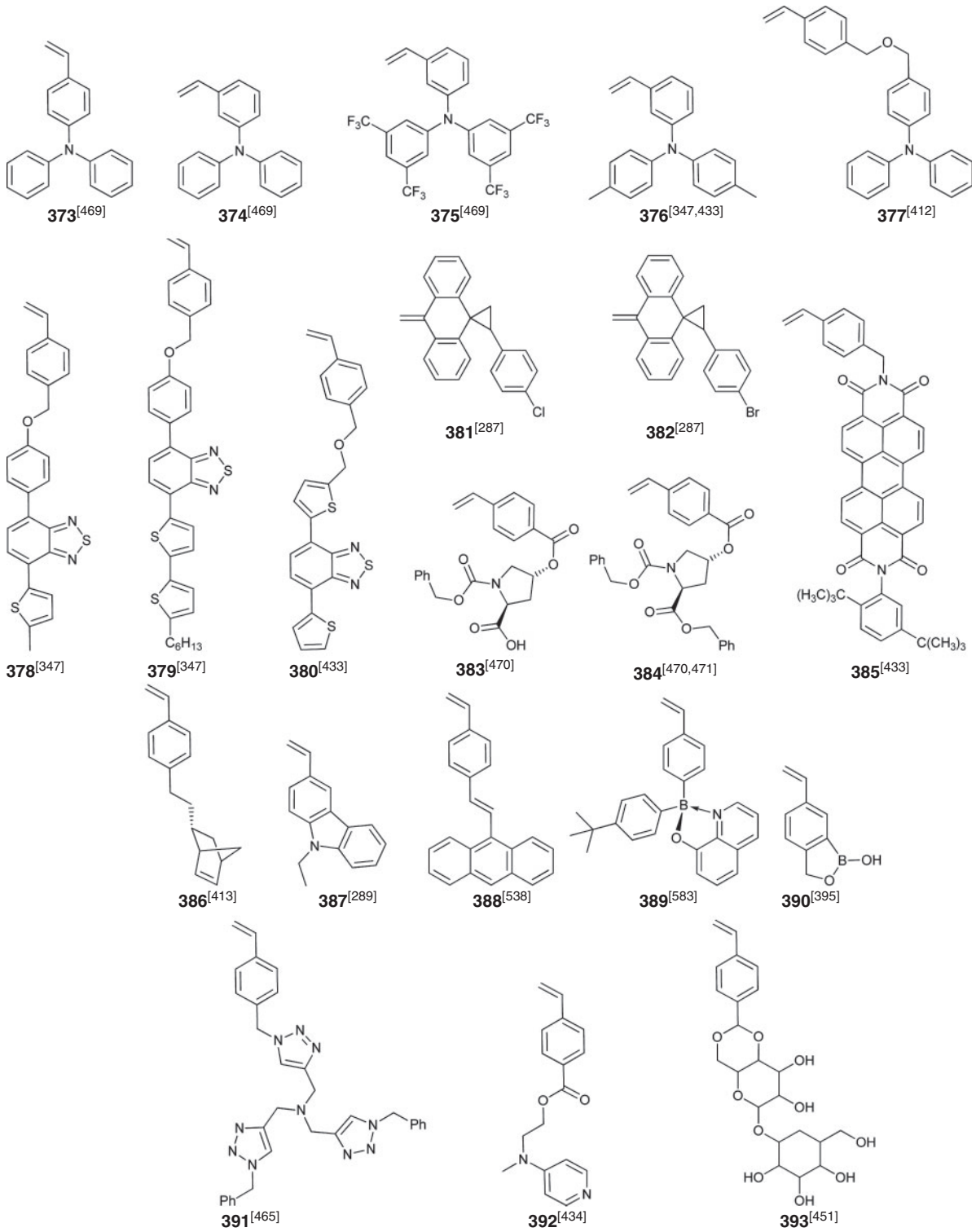


Fig. 9. Styrene derivatives (**373**–**393**) subjected to RAFT polymerization.

Crosslinking Monomers

Crosslinking monomers are used both in the synthesis of microgels and polymer networks (see below). This class of monomer includes DEGDMA, TEGDMA, EGDMA, TEGDA, HDDA, MBAm, DVB, and compounds **418**–**425** (Fig. 16). Use of the monomers such as **420**, with an acetal linkage, and **421**–**423**, with disulfide linkages, results in the formation of degradable crosslinks which can be important in controlled release applications. The crosslinks can also be cleaved to allow polymer analysis. See also the section *Polymer Networks* below.

Cyclopolymerization

Further studies on RAFT cyclopolymerization of DADMAC have been reported. The most recent work used xanthate (**229**)[113,506] or trithiocarbonate (**155**).[440] RAFT polymerization with xanthate (**229**) was controlled although dispersities were broad.[113,506] This was attributed to the low transfer

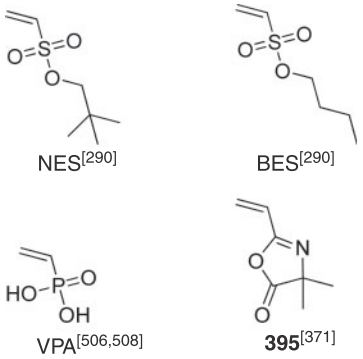


Fig. 10. Vinyl derivatives subjected to RAFT polymerization.

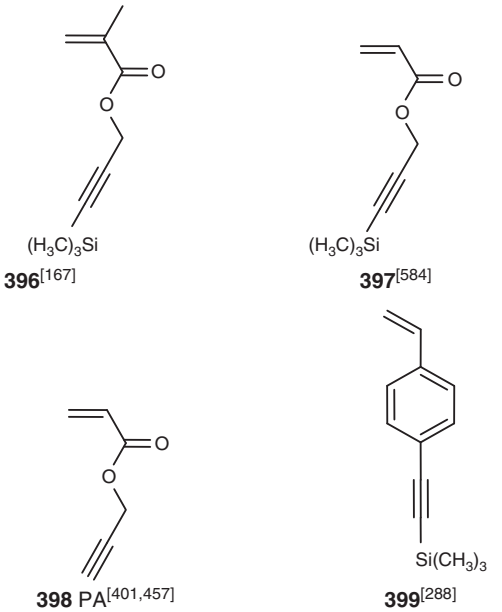


Fig. 11. Alkyne-functional monomers amenable to RAFT (co) polymerization.

constant of poly(DADMAC) macro-RAFT agent in the DADMAC polymerization (Table 1). With trithiocarbonate (**155**), while the polymerization showed some living character, conversions were low and dispersities were poor ($Đ > 1.5$) and the latter increased with monomer conversion.[440] While a trithiocarbonate RAFT agent is likely to have a higher transfer constant in DADMAC polymerization, intermediate radical fragmentation is likely to be slower making retardation more likely.

A 1 : 2 mixture of DVE and MAH with dibenzyl trithiocarbonate was reported to undergo alternating RAFT cyclocopolymerization to provide the polymer **426** as shown in Scheme 6.[341,342] Other studies on RAFT cyclopolymerization are summarized in Fig. 17.

Ring-Opening Polymerization

RAFT ring-opening polymerization provides a simple method of forming polymers with readily cleavable linkages, i.e. esters, thioesters, and/or disulfides, in the carbon–carbon backbone of a polymer chain.[276] The monomers **433**–**437** (Fig. 18) were copolymerized with MMA, DMAm, and HEMA.

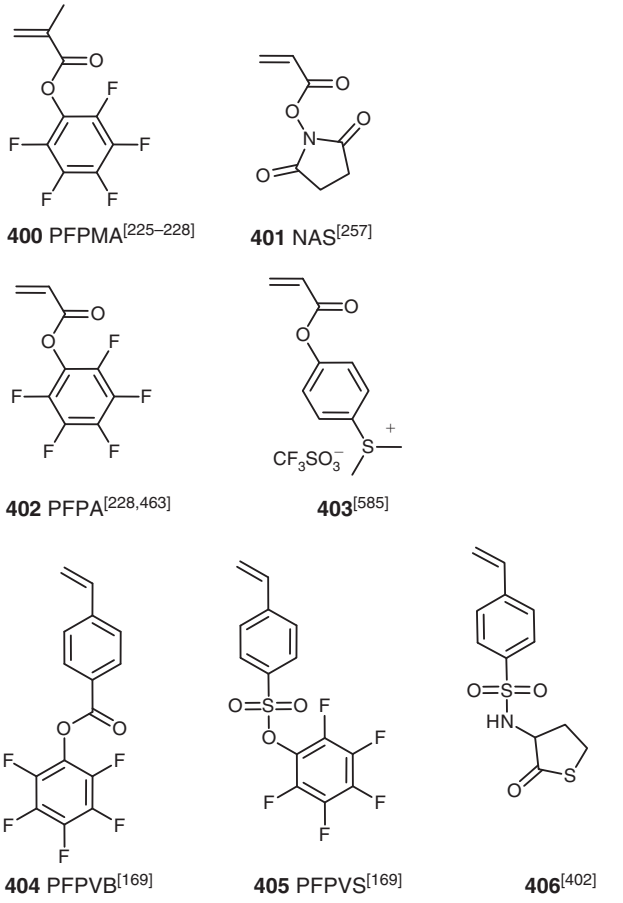


Fig. 12. Monomers with active ester or similar functionality amenable to RAFT (co)polymerization.

End-Functional Polymers and End-Group Transformations

Processes for thiocarbonylthio end-group removal or transformation post RAFT polymerization continue to attract significant interest. Two reviews focussing on end functional polymer and end-group removal/transformation have appeared within the last two years.[33,34] A wide variety of methods are now available for removing or transforming the thiocarbonylthio groups in RAFT-synthesized polymers (Scheme 7[34]). All have advantages and limitations depending on the intended application. The thiocarbonyl functionality present in RAFT-synthesized polymers, once seen as a limitation to the wide-spread adoption of RAFT polymerization can now be seen as an enabling functionality in addressing the needs of the biomedical, optoelectronic, nanotechnology, and other sectors.

Radical-Induced Reduction

Radical-induced reduction allows the thiocarbonylthio group of a RAFT-synthesized polymer to be replaced with a hydrogen atom. Recent examples are shown in Table 16. Selective removal of the dodecyl trithiocarbonate ends from poly(CMS) (with pendant benzylic chloride functionality) was successfully performed with tri-*n*-butylstannane as the H-donor.[436]

Addition–Fragmentation Coupling

A popular method for end-group removal/transformation involves heating the RAFT-synthesized polymer with a large

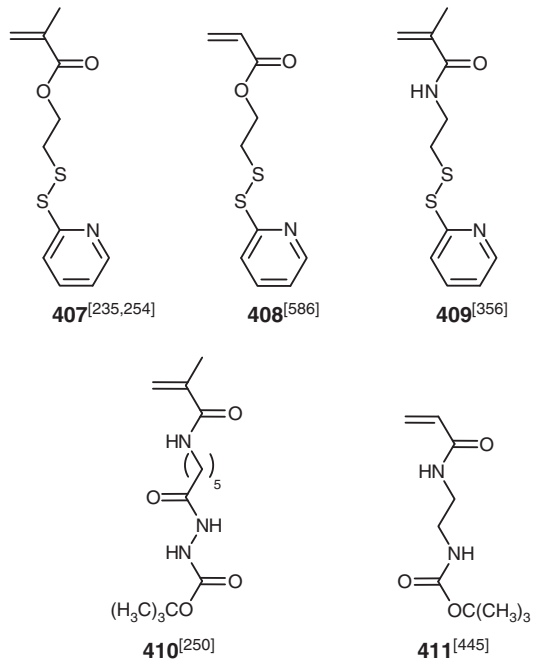


Fig. 13. Monomers with protected thiol, hydrazide or amino functionality amenable to RAFT (co)polymerization.

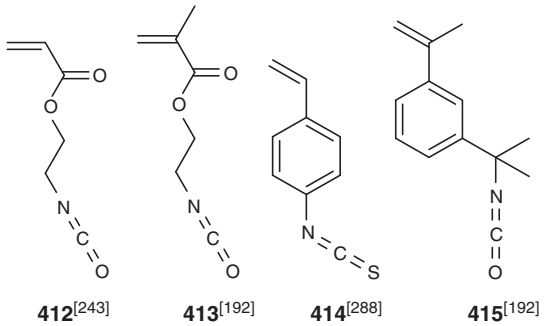


Fig. 14. Monomers with isocyanate or isothiocyanate functionality.

excess of a radical initiator, most often, an azo-compound. That most commonly used is AIBN. However functional azo-compounds (e.g. **438**–**440**, Chart 4) have also been successfully used. Some recent examples are included in Table 17. The strategy appears generally successful for methacrylic polymers (Table 17). The expected complications from primary radical disproportionation are not reported. However, incomplete end-group removal is often found for acrylic and styrenic polymers.[194] The potential limitations of the technology and their causes are discussed in our recent review.[34]

Peroxide initiators (LPO, BPO) have been shown to be generally more effective than azo-initiators (e.g. AIBN) in achieving end-group removal.[593] However, the complication of termination by self reaction of propagating species is more pronounced. Chen et al.[194] have shown that a combination of a peroxide initiator (LPO) and azo-initiator (AIBN) is more effective than either alone (Scheme 8). Since the polymers formed are likely to possess end-groups from the peroxide and the azo-initiator, this strategy is most likely not suitable for preparing polymers with defined end-group functionality. The method has also been used as a degrafting process in silica-supported polymer synthesis.[594]

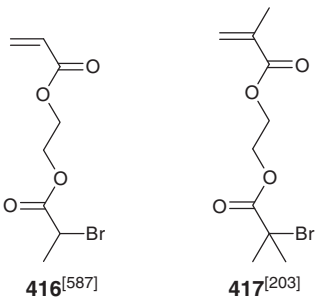


Fig. 15. Monomers with ATRP initiator functionality.

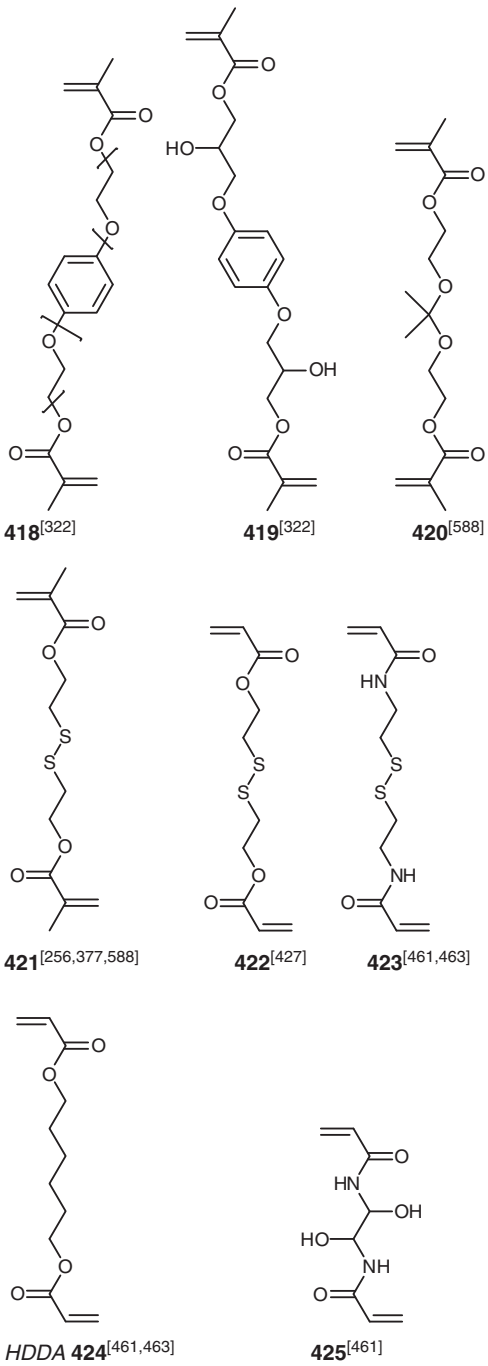
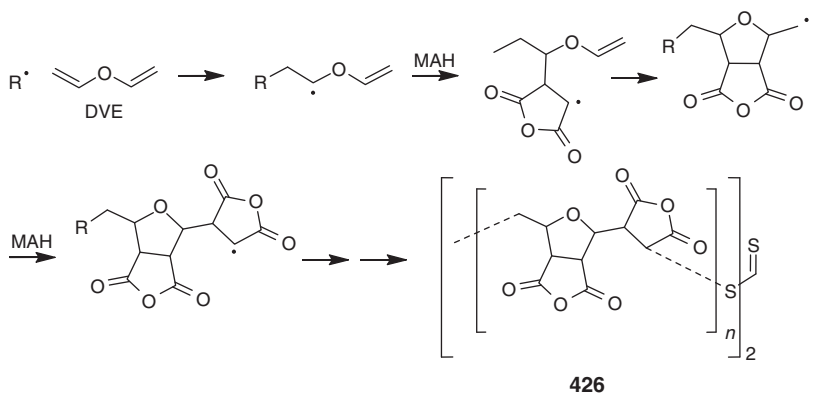


Fig. 16. Crosslinking monomers.



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Scheme 6. RAFT cyclocopolymerization of DVE/MAH.

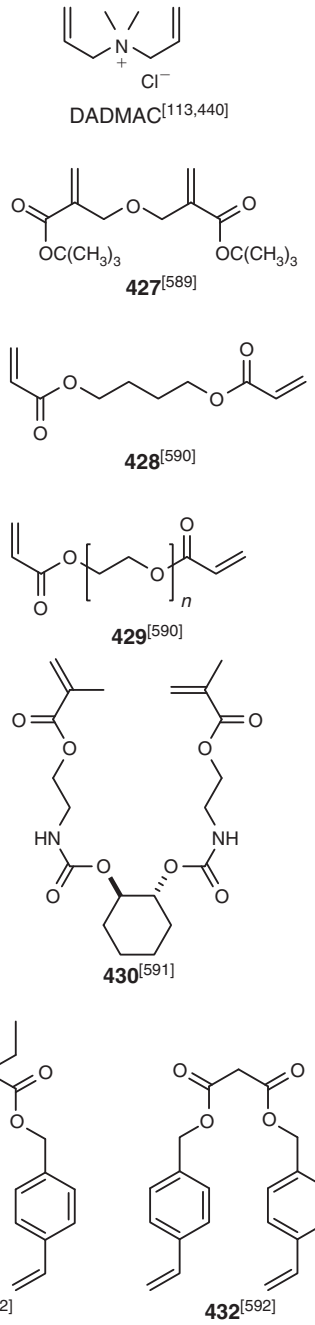


Fig. 17. Monomers subjected to RAFT cyclopolymerization.

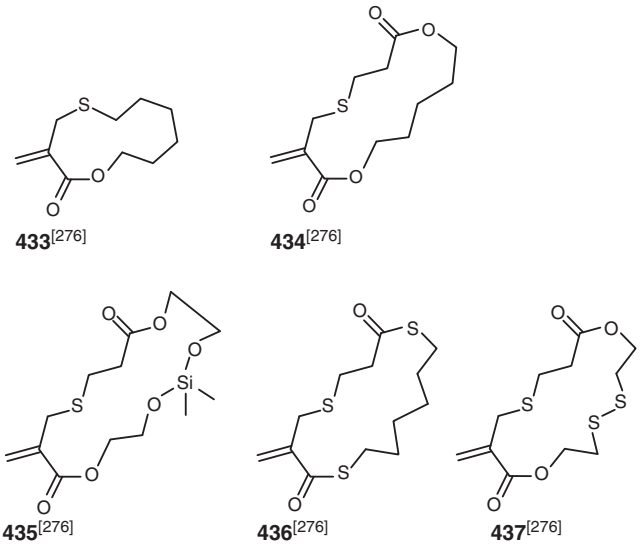


Fig. 18. Monomers subjected to ring-opening (co)polymerization.

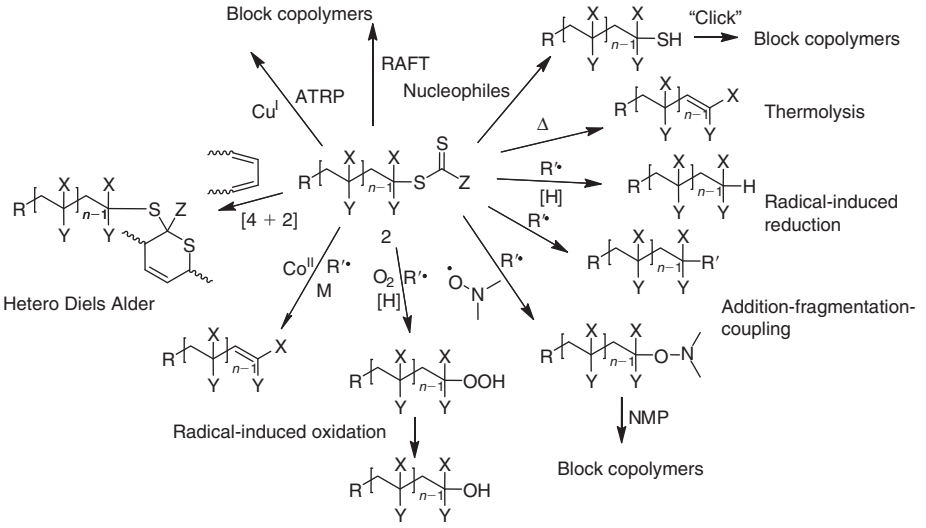
Radical-Induced Oxidation

It has been reported that addition of a very small amount of a CCT agent ($[(CH_3OH)_2Co(dmgBF_2)_2]$: [RAFT agent]$_0 = 1 : 80000$) during the latter stages (~70 % monomer conversion) of a RAFT polymerization of a methacrylate monomer (MMA, BMA) provides complete end-group removal and a high purity low dispersity macromonomer product.[602] Details of the mechanism were not presented, however, a possible mechanism combining elements of those for the RAFT and CCT processes is shown in Scheme 9. The process can be considered as a radical-induced oxidation.

Reaction with Nucleophiles (Aminolysis/Hydrolysis/ Ionic Reduction)

Conversion of thiocarbonylthio end-groups into thiol groups through reaction with nucleophiles is one of the most common end-group transformations. A list comprising recent examples is provided in Table 18. In order to avoid the complication of disulfide formation the process is commonly done in the presence of a reagent to trap the thiol. A summary of the transformations that have been used is provided below (see section entitled *Click Reactions*).[34]

It has been reported that the use of hydrazine as nucleophile is advantageous both in giving a very rapid reaction and little disulfide formation even when the process was carried out in air.[375] However, Lee et al.[176] found disulfide formation to be significant during the hydrazinolysis of St/AcS copolymers.

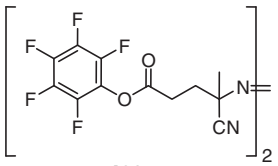


Scheme 7. Processes for RAFT end-group transformation (reproduced from Ref. [34], copyright Society of Chemical Industry). R′• = radical, [H] = H donor, M = monomer.

Table 16. Examples of end-group removal by radical-induced reduction

Terminal monomer unit[A]	Z (initial RAFT agent)	H donor	Ref.
BAm	N-pyrrole	EPHP[B]	[533]
CMS	$SC_{12}H_{25}$	Bu_3SnH	[436]
NVC	OC_2H_5	Bu_3SnH	[514]

[A]Monomer unit adjacent to thiocarbonylthio group. See *Abbreviations*.
[B]EPHP: *N*-ethylpiperidine hypophosphite.



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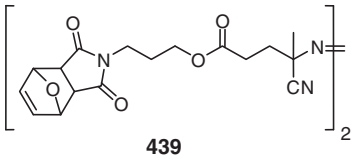

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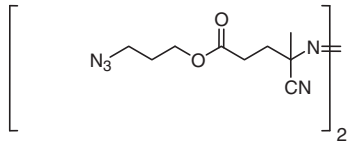

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Chart 4.

Oxidation

Thiocarbonylthio chain-ends of RAFT-synthesized polymers can be efficiently converted into hydroxy chain ends in high yield by heating a THF solution of the polymer and AIBN in air (to produce a polymer with hydroperoxy ends) and then treating this solution with triphenylphosphine.[182,605] The process was demonstrated for polymers with dithiobenzoate or dithiophenylacetate end-groups and for polymers with trithiocarbonate mid-groups (synthesized with dibenzyl trithiocarbonate) (Table 19).

End-groups of poly(MMA) and poly(St) formed with dithiobenzoate **12** are reported to be completely removed by heating a THF solution of the polymer in air.[180] The process was accelerated by addition of acid. The end-group removal process was proposed to involve hydrolysis of the dithiobenzoate to a thiol end-group, however, the end-groups formed were not fully characterized and it seems more likely that the process is analogous to that seen with AIBN/air in THF.

It has also been proposed that hydrogen peroxide can be used to directly transform RAFT end-groups to hydroxy end-groups.[608] The process was applied to poly(NVP) with xanthate chain ends and poly(St) with dithiobenzoate end-groups and involved heating the polymers with hydrogen peroxide at 60°C. The proposed mechanism involved thermal generation of hydroxyl radicals and an addition-fragmentation-coupling process (see below). However, while hydrogen peroxide may undergo induced decomposition, thermal homolysis requires relatively high temperatures.

A facile process in which alkaline hydrogen peroxide is used to transform dithioesters (ZCS_2R) to a mixture of a carboxylic acid (ZCO_2H) and a disulfide (RSSR) in very high yield has been reported[609] but has not been applied to polymeric substrates.

The radical-induced (radicals from AIBN) air oxidation of RAFT agents and RAFT-synthesized polymers has been investigated by Li et al.[162] The rate of oxidation was greatest for bulky or electron-deficient 'R'. For a given 'R' group, the ease of oxidation of RAFT agents appeared to have an inverse correlation with the activity of the RAFT agent in polymerization and increased in the series where 'Z' is phenyl– < benzyl– (dithioesters) < alkylS– (trithiocarbonates) < alkylO– (xanthates). The main reaction observed for all classes of RAFT agent was replacement of the thiocarbonyl group with a carbonyl group. This reaction accounts for some loss of living character during RAFT polymerization in air.

Table 17. Examples of end-group removal by addition-fragmentation-coupling

Terminal monomer[A]	Z[B]	Initiator	[Initiator]/[RAFT][C]	Temperature	Percentage of ends removed[D]	Ref
MMA	Poly(MMA)S	AIBN	100	80	100	[320]
PFPMA	Ph	AIBN	25	70	100	[225]
PFPMA	Ph	AIBN	30	78	100	[227]
TEGMA	Ph	ACPA	30	78	100	[227]
PFPMA/LMA	Ph	AIBN	25	70	100	[225]
BA	Ph	AIBN	30	80	<25	[194]
HA	Ph	ACPA	5	70	100	[240]
HA	Ph	AHPN	5	70	100	[240]
BA/NA	Ph	AIBN	20	80	100	[202]
BA	C_4H_9S	AIBN	30	80	<25	[194]
BA	C_4H_9S	AIBN + BPO	20 + 2[E]	80	100	[194]
HPA	$C_{12}H_{25}S$	AIBN	10	80	(100)[F]	[595]
HPA	$C_{12}H_{25}S$	BPO	10	80	100	[595]
2EHA	Ph	T21S	20	80	100	[596]
tBA	Poly(tBA)S	AIBN	–	80	100	[597]
NIPAm	Poly(tBA-*b*-NIPAm)S	AIBN	–	80	100	[597]
tBA/TBBPMA	Ph	AIBN	(20)	(80)	100	[598]
DAMEA/TFEA	$C_{12}H_{25}S$	AIBN	20	65	100	[599]
HADA/MADA/NLAA	$C_{12}H_{25}S$	AIBN	20	60	100	[403]
OEGMA	Ph	AIBN	30	80	100	[600]
OEGMA	Ph	**439**	30	80	100	[600]
LMA	Ph	AIBN	30	80	100	[601]
NIPAm	C_2H_5S	**440**	100	70	100	[454,483]
HADM/MADM/NLAM	Ph	AIBN	20	60	100	[403]
HPMAm/APMAm	Ph	AIBN	20	70	100	[251]
HPMAm	Ph	**441**	20	70	100[G]	[255]
St	Ph	AIBN	20 – 100	80	<80	[194]
St	Ph	AIBN + BPO	20 + 2[E]	80	100	[194]
St	C_4H_9S	AIBN	30 – 100	80	<60	[194]
St	$C_{12}H_{25}S$	AIBN	10	95	92	[393]

[A]Monomer unit adjacent to thiocarbonylthio group.
[B]'Z' group of RAFT agent or macro-RAFT agent.
[C]Mole ratio of initiator to RAFT synthesized polymer.
[D]Percentage of end-groups removed. Where details of polymer characterization were not provided the values appear in parentheses.
[E]A mixture of AIBN and BPO was used.
[F]Bimodal distribution observed for higher reaction temperatures (>80°C).
[G]Complete end-group removal but combination product seen as by-product.

RAFT-synthesized polymers with xanthate end-groups react with ozone quantitatively to form the corresponding polymer with a thiolocarbonate end-group.[606,607] The mechanism was not fully elucidated but the thiocarbonyl is replaced with a carbonyl and sulfuric acid is formed as a by-product (Scheme 10). The process was claimed to also be applicable to other RAFT end-groups (trithiocarbonates, dithioesters) and a patent was filed on the use of this process.[607]

Thermolysis

An in depth study of the mechanism of thermal decomposition of RAFT agents in solution has appeared.[610] The thermal stability of dithiobenzoates was found to decrease in the series where R is $CH_2Ph > poly(St) > CH(CH_3)Ph > C(CH_3)_2C_2OC_2H_5 > C(CH_3)_2Ph > poly(MMA) > C(CH_3)_2CN$. The thermal stability of RAFT agents with R = phenylethyl decreased in the series where Z is $OC_2H_5 > N(C_2H_5)_2 > SCH(CH_3)Ph > Ph > CH_2Ph > PhNO_2$. Some correspondence with activity (C_{tr}^{app} value) was noted. For RAFT agents possessing β-hydrogens the mechanism of decomposition was proposed to involve Chugaev elimination.

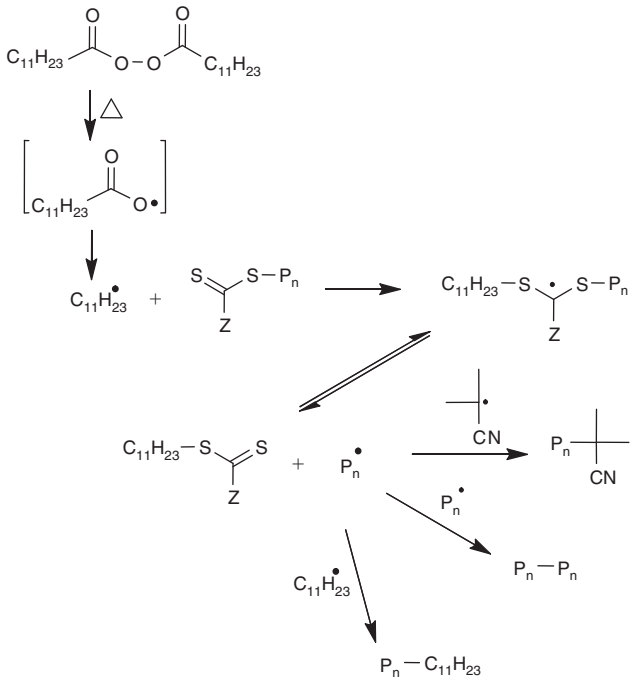
End-group thermolysis has usually been carried out at temperatures >150°C for relatively short reaction times. It has been reported that thermolysis of poly(MMA)-dithiobenzoate in dimethyl sulfoxide solution is complete after heating at 100°C for 24 h.[183] The unsaturated end-group produced was subsequently transformed by thio-Michael reaction with mono(6-deoxy-6-mercapto)-β-cyclodextrin.

Click Reactions

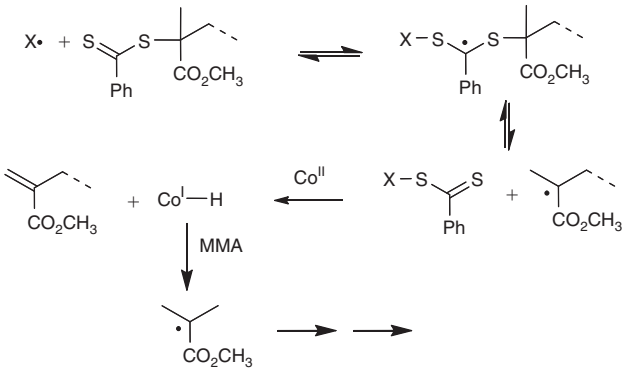
Use of 'click chemistry' in combination with RAFT polymerization continues to attract much attention.[38,66–68] The RAFT process can be used to synthesize polymers with clickable moieties at the chain ends through the use of RAFT agents with appropriate functionality on 'Z' or 'R'.

Some reactions in this category are:

- Copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition. Recent examples of RAFT agents prepared or used that contain an alkyne functionality include dithiobenzoates **22**,[255] **28**, and **33**,[259] trithiocarbonates **118**,[379] **136**,[267] and **161**,[442] and xanthate (**231**).[518] Those incorporating azide functionality include trithiocarbonates **102**,[371] **137**,[371] and **138**.[419] Examples of the use of this form of click reaction include the synthesis of poly(NIPAm) stars based on a hexakis(fullerene) core.[267] Pressley et al.[611] have reported on an improved methodology for conducting click reactions to form block and cyclic polymers.



Scheme 8. Addition–fragmentation-coupling (AIBN + LPO initiator).



Scheme 9. RAFT – catalytic chain transfer process.

The process makes use of commercially available copper nanoparticles and is performed with microwave irradiation. The process was claimed to be insensitive to air.

- The active ester-amine reaction. RAFT agents with active ester functionality include dithiobenzoate **25**[259] and trithiocarbonates **130**[386] and **181**[466].
- The thiol-halide reaction. The dibromomaleimide group (e.g. **177**) has been shown to react with thiols under mild reaction conditions and does not need to be protected during RAFT polymerization of acrylates and acrylamides.[459] Significant retardation was observed with use of **177** in St polymerization.

The thiocarbonylthio functionality can be transformed to a thiol group through reaction with nucleophiles (see above). A variety of thiol transformation reactions, some of them referred to as 'click' processes, can then be used. These include the thiol-ene reaction and other processes as shown in Scheme 11.[34,35] Thiol-click reactions have been reviewed[71] and references to some recent examples of these process are included in Table 18.

A detailed study of the thiol-ene based Michael addition reactions has been reported[612] in which various catalysts, primary and tertiary amines, and phosphines, were investigated for the reaction of thiols with dimeric and oligomeric (meth) acrylate macromonomers. While primary and tertiary amines were effective catalysts for the thiol–ene reaction, several hours were required to reach high conversions. The phosphine catalysts, dimethylphenylphosphine (DMPP) and tris-(2-carboxyethyl)phosphine (TCEP), were more efficient. DMPP provided complete conversion within a few minutes under optimized conditions. However, the concentration of DMPP had to be kept at very low levels to avoid the formation of by-products originating from the addition of DMPP to the macromonomer. TCEP was an efficient catalyst for thiol-ene reactions in aqueous media when the pH of the medium was higher than 8.0. Under acidic pH the formation of by-products was observed.

An in-depth study of the thiol-epoxy reaction for end-group modification of poly(DEAm) and poly(St) prepared with a dithiobenzoate RAFT agent (**18**) has appeared.[193] The use of both base (DBU) and Lewis acid catalysis was studied.

A third class of reaction involves direct modification of the RAFT thiocarbonyl functionality:

The Thiocarbonyl-Hetero-Diels Alder Reaction

RAFT agents and macro-RAFT agents with electron withdrawing 'Z' undergo hetero-Diels Alder reactions with suitable dienes (Scheme 12).[268,546,613,614] In recent work the process has been developed as a route to block copolymers,[268,296,297,548,615] graft, star, and network polymers,[309,614] and modified surfaces.[295,547,613] The method is also used in synthetic organic chemistry.[616] The process requires RAFT agents or macro-RAFT agents with an electron withdrawing 'Z' group. Suitable 'Z' groups include 2-pyridyl (**57**, **70**), phosphonate (**282**–**284**), or phenylsulfonyl (**280**). To achieve acceptable rates for reactions in organic solution, the reaction may be catalyzed by a Bronsted or Lewis acid, for example, trifluoroacetic acid or zinc chloride. However, for reaction in aqueous solution no catalyst is necessary.[297] The reaction is thermally reversible[309,548,617] prompting a proposal that it might be used as a thermally stimulated colour switch[548,617] or be applied in reversible block[298] or network formation.[309]

The Thiocarbonyl 1,3-Dipolar Cycloaddition Reaction

It has been found that diazomethane undergoes a facile 1,3-dipolar cycloaddition with dithiobenzoate RAFT agents and with dithiobenzoate end-groups of polymers formed by reversible addition–fragmentation chain transfer (RAFT) polymerization.[181] Thus, 2-cyanoprop-2-yl dithiobenzoate (**12**), on treatment with diazomethane at room temperature, provided stereoisomeric 1,3-dithiolanes in near quantitative (>95 %) yield. A low molar mass RAFT-synthesized poly(MMA) with dithiobenzoate end-groups underwent similar reaction as indicated by immediate decolourization and a quantitative doubling of molar mass. Higher molar mass poly(MMA) were also rapidly decolourized by diazomethane and provided a product with a bimodal molar mass distribution. Under similar conditions, the trithiocarbonate group does not react with diazomethane. The proposed mechanism is shown in Scheme 13.

Other End-Group Modification Processes

Staudinger ligation has been proposed as a method for quantitative end-group modification with possible application in

Table 18. Examples of conversion of thiocarbonylthio end-groups to thiol end-groups through reaction with nucleophiles

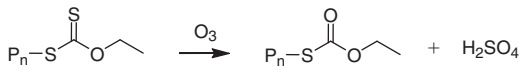
Terminal monomer unit[A]	Z (initial RAFT agent)	Reagent[B]	Comment	Ref
MA, NIPAm	Ph	Hexylamine	In situ thio-bromo click	[241]
MMA, St	**456**	Propylamine	Network cleavage	[603]
BA, St	**441**	Butylamine/TCEP/BA	In situ thiol-ene multiblock cleavage	[604]
PEGA	**47**	Butylamine/TCEP/divinyl sulfone	In situ thiol-ene	[281]
MA, DMAm, NIPAm, St,	C_2H_5S (**121**)	Hydrazine	–	[375]
St, PEGMA	Ph (**54, 18**)	Hydrazine	–	[375]
St	Ph (**18**)	Hydrazine	Used in thiol-epoxide	[193]
St	Ph (**18**) DEAm (**18**)	Hydrazine	In situ thiol-epoxide	[193]
St/AcS	Ph (**11**)	Hydrazine	Au nanoparticles	[176]
EGDMA, **421, 420**	Ph (**18**)	Hexylamine	Used in thiol-ene or other reaction	[588]
St	$PhCH_2S$	1) KOH, 2) Zn/AcOH	Au nanoparticles	[338]
St	$PhCH_2S$ (**89**)	Ethylene diamine	Initiator for ROP[C]	[339]
HPMAm	Ph (**11**)	$NaBH_4/PBu_3$	In situ thiol-ene (AA)	[161]
HPMAm	Ph (**68**)	Butylamine	MeOH/degassed used in thiol-ene	[307]
NIPAm	Ph (**18**)	$NaBH_4$	Used in thiol-ene	[247]
MMA	Ph (**18**)	Hexylamine	In situ thiol-ene	[220]
HPMAm	Ph (**18**)	Hexylamine	In situ thiol-ene	[220]
NIPAm	$CH_2(CO_2H)CH_2S$ (**179**)	Hexylamine	In situ thiol-ene	[220]
NIPAm	C_4H_9S (**159**)	Hexylamine/DMPP	Used in thiol-ene	[446]
NIPAm	$C_{12}H_{25}S$ (**123**)	Hexylamine/Bu_3Ph	Used in thiol-ene	[398]
Am	Ph (**18**)	$NaBH_4$	Used in thiol ene	[244]
DEAm	Ph (**38**)	Propylamine/DMPP	Initiator for ROP[D]	[273]

[A]Monomer unit adjacent to thiocarbonylthio group.
[B]TCEP – tris-(2-carboxyethyl)phosphine, DMMP – dimethylphenylphosphine.
[C]Thiol used as initiator in ring-opening polymerization of lactide.
[D]Thiol used as initiator in ring-opening polymerization of *N*-carboxyanhydride.

Table 19. Examples of oxidation of thiocarbonylthio end-groups

Terminal monomer[A]	Z[B]	Reagent(s)	Comment	Product end-group	Ref.
StMe	OEt	Ozone	–	–(C=O)SOEt	[606]
BA	OEt	Ozone	–	–(C=O)SOEt	[607]
iBoA	2-pyridyl	Air	AIBN, THF/Ph_3P	–OH	[605]
MMA, acrylates	Ph	Air	AIBN, THF/Ph_3P	–OH	[182,605]
St, acrylates	P_nS	Air	AIBN, THF/Ph_3P	–OH	[182]
MA, BA	CH_2Ph	Air	AIBN, THF/Ph_3P	–OH	[182]
St	CH_2Ph	Air	AIBN, THF/Ph_3P	–OH	[319]
St	Ph	H_2O_2	–	–OH	[608]
NVP	OEt	H_2O_2	–	–OH	[608]

[A]Monomer unit adjacent to thiocarbonylthio-group.
[B]'Z' group of RAFT agent or macro-RAFT agent.



Scheme 10. Reaction of xanthates with ozone.

forming bioconjugates.[370] RAFT agents **99**–**101** and **129** were prepared to test the hypothesis. The phosphine functionality in these RAFT agents did not interfere in the RAFT polymerization. For poly(St) formed with **99**, Staudinger ligation appeared slow. For poly(St) formed with **100**–**129**, while Staudinger ligation appeared rapid and quantitative, the sensitivity of the phosphine group to oxidation, even when borane-protected, was found to be a complication.[370]

Statistical/Gradient Copolymers

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

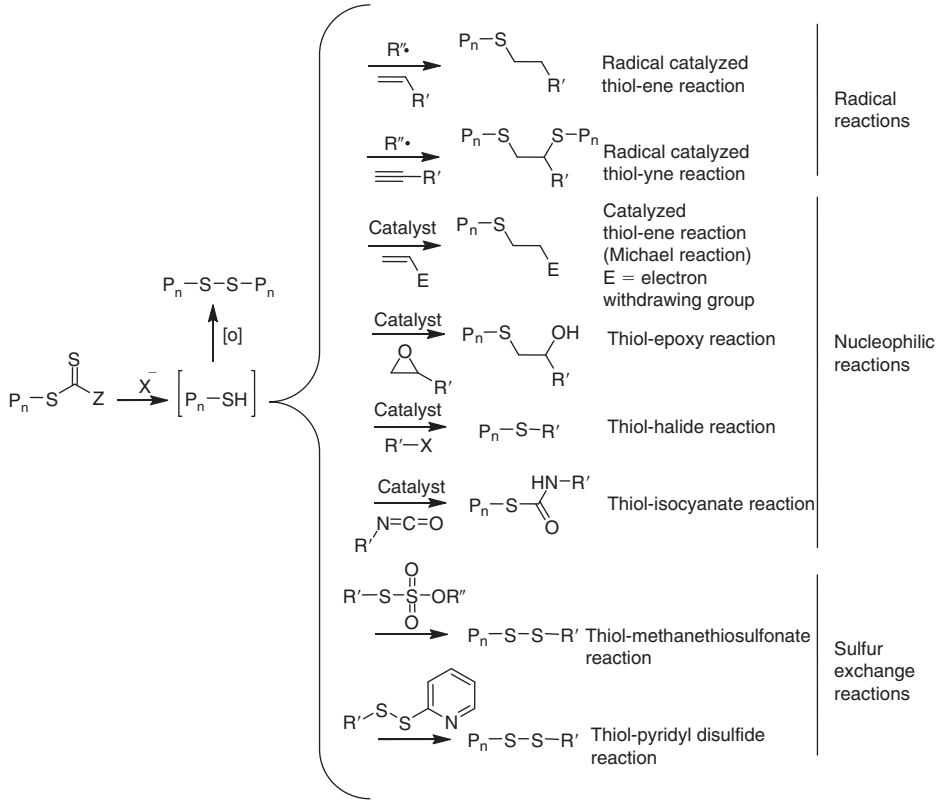
Block Copolymers

Sequential Monomer Addition

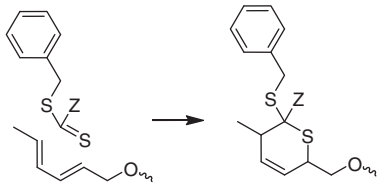
Examples of block copolymer synthesis by sequential monomer addition are included in Tables 3–14. See also the section *Choice of RAFT Agents* for discussion and results on the importance of choosing which monomer to polymerize first and on the use of switchable RAFT agents in this context.

ATRP-RAFT

Thiocarbonylthio compounds have found use as initiators in ATRP.[44] The first reports involved the use of *N*,*N*-dialkyl dithiocarbamate derivatives as ATRP initiators. Dithiocarbamates do not provide effective control over the polymerization



Scheme 11. Reactions of RAFT end-group with nucleophiles with trapping of the thiol end-group formed (Reproduced from Ref. [34], copyright Society of Chemical Industry).



Scheme 12. The thiocarbonyl hetero-Diels Alder Process.

of MAMs (e.g. St, MMA, MA, AN) in the RAFT process so the control mechanism is most likely that of ATRP.

Recently, more active RAFT agents such as *N*,*N*-diaryldithiocarbamates, 1-pyrrolecarbodithioates, trithiocarbonates,[387] and dithioesters (1-dithionaphthalates[206] and dithiobenzoates[168]) have been used as initiators in these polymerizations.[44] Since these are effective RAFT agents with the monomers used, it is pertinent to question the mechanism of the process. While one should not exclude ATRP participation, it seems best to consider these processes as RAFT polymerizations with ATRP initiation. The combination of zero-valent iron (iron powder) and dithioester **16** was used to initiate RAFT polymerization and this may involve a similar mechanism.[205]

Further examples of the synthesis of polymers by a combination of ATRP and RAFT have been reported.[185,525,618] This can involve preparing one block comprising a MAM by ATRP and then a second block comprising a LAM by RAFT.

Matyjaszewski and co-workers have used compounds that combine RAFT agent and ATRP initiator functionality in the one molecule in the synthesis of poly(NVP) blocks (Scheme 14).[525] Bromoisobutyrate derivatives (e.g. **241**, successful with VAc) could not be used as RAFT agents in this context because of dimerization of NVP which was catalyzed by trace amounts of HBr.[525] This problem was overcome with the use of the corresponding chloroisobutyrate (**242**).

Further examples of coupling of RAFT-synthesized polymers with ATRP-synthesized polymers by copper-catalyzed click reaction have also been reported.[416]

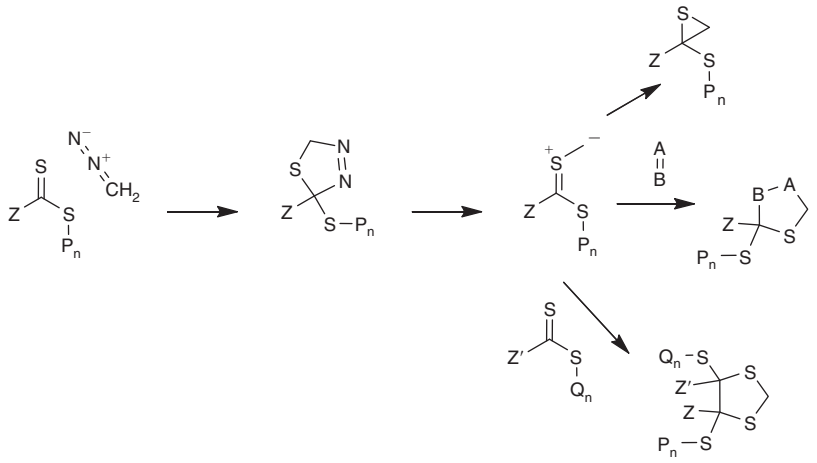
NMP-RAFT

RAFT end-group transformation by addition–fragmentation-coupling can be performed in the presence of a nitroxide to yield an alkoxyamine chain end.[619] This enables macro-RAFT agents to be transformed to alkoxyamines for use in NMP. Favier et al.[619] developed such a process for exchanging the thiocarbonyl group (ZC(=S)S–) of macro-RAFT agents with a nitroxide (R'_2NO–) (Scheme 15), which they termed ESARA; an acronym for 'exchange of substituents between (macro) alkoxyamines and (macro)RAFT agents'. The process was demonstrated for low molar mass RAFT agents or macro-RAFT agents and SG1-based alkoxyamines.

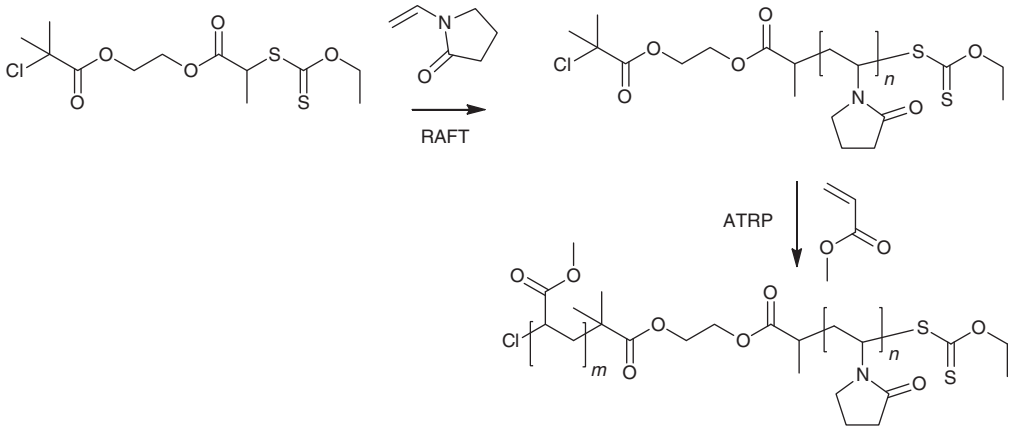
The dithiobenzoates RAFT agents **45** and **46** are also TEMPO-based alkoxyamine initiators for NMP.[280] These agents provided reasonable control over polymerization of St under RAFT conditions (60°C, AIBN initiator) for low monomer conversions although dispersities broadened for higher monomer conversions. Poor control was observed in St polymerization under 'NMP conditions' (120°C). Good control ($Đ < 1.3$) was observed for PEGMA and NIPAm under RAFT conditions but poor control ($Đ > 1.7$) for AA and tBA under RAFT conditions. Block copolymer formation was also examined.

ROP-RAFT

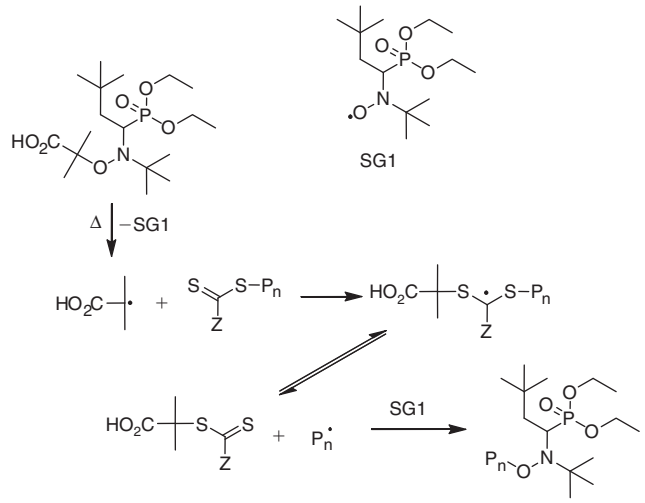
Hydroxy-end functional polymers prepared by RAFT polymerization can be used as initiators in ring-opening



Scheme 13. Thiocarbonyl 1,3-dipolar cycloaddition reaction.



Scheme 14. ATRP/RAFT combination for block copolymer synthesis.



Scheme 15. ESARA – exchange of substituents between (macro)alkoxyamines and (macro)RAFT agents.

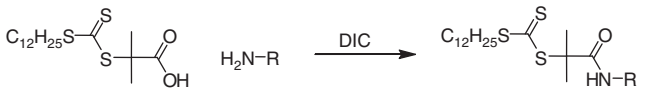
polymerization of cyclic esters (e.g. caprolactone, lactide). Three different strategies have recently been reported. These involve:

- the use of hydroxy end-functional poly(NIPAm/DMAm) prepared with RAFT agent **37** to prepare low dispersity poly(NIPAm/DMAm)-*block*-PLA.[270–272]
- the use of trithiocarbonate **140** to carry out simultaneous RAFT polymerization of St and ROP of lactide.[421] The product was used as a macromonomer in ROMP.
- transformation of the end groups of poly(St) prepared with phenyldithioacetates **77** or **78** to hydroxy groups by oxidation. Thsese polymers were then used to initiated ROP of caprolactone.[319]

Table 20. Macro-RAFT agents formed from acid functional RAFT agents

Acid RAFT agent	Block A[A] (end-group)	Reagents[B]	Macro-RAFT agent	Block B[C]
Block				
18	Oligopeptide (NH_2 end)	DIC/HOBT	–	HPMAm[255,307]
–	PDMS (OH end)	DCC/DMAP	**149**	MMA[431]
123	PEP-*b*-PEO (OH end)	Oxalyl chloride	–	NIPAm[620]
123	PLA (OH end)	Oxalyl chloride	**133**	**377**[412] St/**386**[413]
123	PIP (NH_2 end)	Oxalyl chloride	**143**	tBA[424]
98	SN38[D]	DIC/DMAP	–	HPMAm[621]
Graft				
123	Brush with PLA (OH end)	Oxalyl chloride	–	St[305]

[A]Substrate used in forming macro-RAFT agent. PEP – hydrogenated poly(isoprene).
[B]DIC – diisopropyl carbodiimide, DCC – dicyclohexyl carbodiimide, HOBt – 1-hydroxybenzotriazole, DMAP – 4-(dimethylamino)pyridine.
[C]Monomer polymerized in the presence of Block A macro-RAFT agent.
[D]7-Ethyl-10-hydroxycamptothecin.



Scheme 16.

Macro-RAFT Agent Synthesis

Block copolymers based on polymers formed by other polymerization mechanisms are often made by first preparing an end functional pre-polymer which is converted into a macro-RAFT agent by end-group transformation. This macro-RAFT agent is then used in the preparation of the desired block copolymer. Some examples of macro-RAFT agents are shown Tables 3–14 and include PEO macro-RAFT agents (**21**, **119**, **120**, **132**, **169**, **245**), PCL macro RAFT agents (**66**, **225**), a PLA macro-RAFT agent (**133**), polybenzamide macro-RAFT agents (**59**, **60**), polyisoprene macro-RAFT agents (**143**, **200**), a PDMS macro-RAFT agent (**148**), and poly(3-hexylthiophene) macro-RAFT agents (**75**, **116**, **152**, **184**, **185**). Other examples are mentioned in Table 20. The use of protein-derived macro-RAFT agents has been reviewed.[60]

Esterification/Amidation

A frequently used approach involves esterification or amidation of a substrate possessing amino- or hydroxy-functionality with a carboxy-functional RAFT agent (e.g. Scheme 16). Examples of this strategy are summarized in Table 20.

Single Unit Monomer Insertion

Another strategy for preparing macro-RAFT agents involves insertion of a macromonomer unit into a small RAFT agent. The strategy involves careful selection of monomer or reaction conditions such that there is no oligomerization. The strategy has been applied to form poly(3-hexylthiophene) macro-RAFT agent **152**.[62,433]

Halogen Substitution

The hydroxyl end-group of PCL formed by ring-opening polymerization was transformed to a xanthate chain end by sequential reaction with 2-bromopropionyl bromide and potassium xanthate, and the resultant macro-RAFT agent used in RAFT polymerization of NVP.[497] For other examples of forming macro-RAFT agents by halogen substitution see *ATRP-RAFT* above.

Click Reactions

RAFT agents with functionality for use in various 'click' reactions have been reported and have been used to form macro-RAFT agents. These RAFT agents include those with active ester or thiazolidine-2-thione functionality for reaction with amine functional substrates, with alkyne or azide functionality (for use in copper catalyzed cycloaddition), or with various thiol reactive groups.

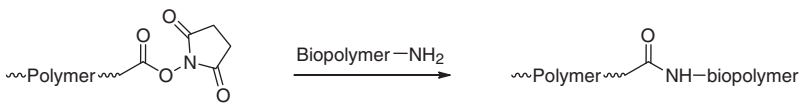
Sumerlin and co-workers[406] prepared a macro-RAFT agent by conjugation of RAFT agent **131** (with active ester functionality) with free amino groups of lysozyme. This was used in RAFT polymerization to attach poly(NIPAm)-*b*-poly(DMAm) by sequential monomer addition. In another study they[420] prepared a macro-RAFT agent by conjugation of a RAFT agent having ene-functionality (**140**) to a free thiol group of bovine serum albumin (BSA). This was used in RAFT polymerization to attach a poly(NIPAm) block.

Biopolymer Conjugates Post-RAFT Polymerization

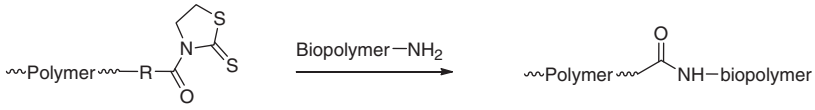
Interest in the synthesis of block and graft copolymers (conjugates) with biological polymers continues unabated. Methods for preparing biopolymer conjugates have been reviewed.[53,54,57,89] The most common method involves coupling the RAFT-synthesized polymer with the biopolymer through reactive functionality present on either the 'R' or 'Z' groups. Note that use of functionality on 'Z' leaves the thiocarbonylthio group as a potentially degradable link at the block juncture. This may or may not be advantageous depending on the application. Most of the methods for conjugation have already been mentioned under end group transformation. They include the active ester–amine reaction, the thiazolidine-2-thione–amine reaction, the pyridyl disulfide–thiol reaction, and the thiol-ene or thio Michael reaction.

a) The Active Ester–Amine Reaction (Scheme 17)

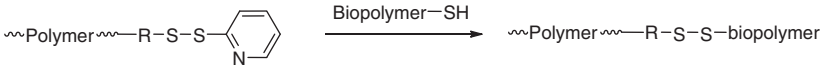
This usually involves the use of a biopolymer (e.g. a protein) with primary amine groups and a RAFT-synthesized polymer bearing an active ester substituent. RAFT agents with active ester functionality include **25**[259] and **130** (used to prepare poly (NIPAm) for conjugation with lysozyme).[386] The active ester may also be formed post-RAFT polymerization from a RAFT-synthesized polymer with a carboxy end-group.[382] Many studies have shown that active ester groups such as those present in **25** and **130** are substantially more reactive than the RAFT agent thiocarbonyl functionality and conditions can be found



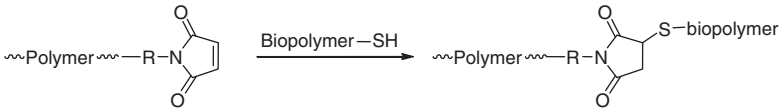
Scheme 17. The active ester–amine reaction.



Scheme 18. The thiazolidine-2-thione–amine reaction.



Scheme 19. The pyridyl disulfide–thiol reaction.



Scheme 20. The thiol-ene reaction.

such that the active ester–amine reaction occurs to the exclusion of any thiocarbonylthio aminolysis. Nonetheless, a potential issue with this chemistry is that primary amines may react with the RAFT agent functionality instead of or as well as the active ester functionality. Similar concerns exist in the case of the thiazolidine-2-thione-amine reaction below.

b) Thiazolidine-2-thione–Amine Reaction (Scheme 18)

RAFT agents with thiazolidine-2-thione functionality include **24**,[238] **107**,[372] **109**,[376] and **195** (used to prepare poly(HPMAm) for conjugation with lysozyme)[372] and **108** (used to prepare poly(PEGMA) for conjugation with lysozyme).[374] Comments are similar to those for the active ester amine reaction.

c) Pyridyl Disulfide–Thiol Reaction (Scheme 19)

This usually involves reaction between a RAFT-synthesized polymer bearing a pyridyl disulfide functionality with a thiol-functional biopolymer (e.g. a cystein residue). RAFT agents with pyridyl disulfide functionality include **86** (used to prepare poly(PEGA) to conjugate a thiol-functional peptide),[334] **164** (used to prepare poly(PEGA) to conjugate siRNA[452] and poly(NIPAm) which was coupled to glutathione[453]) **163** and **165** (used in preparing a trehalose glycopolymer which was coupled with a thiolated lysozyme), and **194** (used to synthesize poly(HPMAm) and thereby form a mid chain conjugate with BSA).[477] This pyridyl disulfide functionality is compatible with RAFT polymerization and most monomers. The pyridyl disulfide group can also be introduced post-polymerization by transformation of the RAFT end-group (see *Click Reactions*).

d) Thiol-ene or Thio-Michael Chemistry (Scheme 20)

The strategy involves some initial RAFT end-group transformation. The reactivity of thiol and ene functionality in radical polymerization is such that it must be introduced post-RAFT polymerization. Polymers with a thiol end groups can be formed by any of the methods mentioned above and conjugated to an ene-functional biopolymer. However, the alternative process of coupling an ene functional polymer with a thiol-functional biopolymer is more attractive because the greater availability of the latter.

Examples of conjugate formation are:

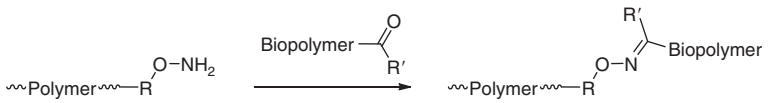
- the reaction of poly(NIPAm) with a thiol end-group with maleimide-functional DNA.[247]
- the reaction of poly(Am) with a thiol end-group with maleimide-functional oligodeoxyribonucleotide.[244]
- thio-Michael reaction of poly(NIPAm) having a thiol end-group with a bis-maleimide to provide a poly(NIPAm) bearing a maleimide end-group. This, in turn, was used in a second thio-Michael reaction with the thiol functionality of albumin (BSA) or ovalbumin (OVA).[398]
- trapping the aminolysis product poly(PEGA) dithiobenzoate with divinyl sulfone and using this in a second thio-Michael reaction with the thiol functionality of albumin (BSA).[281]
- the thiol end-group of poly(BzMA)-*b*-poly(HPMA) was reacted in situ with AA in a thio-Michael process to form a carboxy-terminated polymer which was conjugated to an amine-functional folate derivative by DCC coupling.[161]

e) Aminooxy-Ketone/Aldehyde Reaction (Scheme 21)

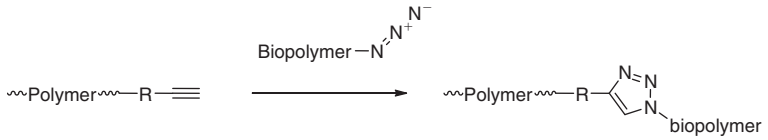
RAFT agents with BOC-protected aminooxy functionality include **85**[334] and **131**.[408] Vázquez-Dorbatt et al.[408] exploited the aminooxy-ketone/aldehyde reaction for preparing protein conjugates to poly(NIPAm) prepared with **131**.

f) Azide-Alkyne Click Reaction (Scheme 22)

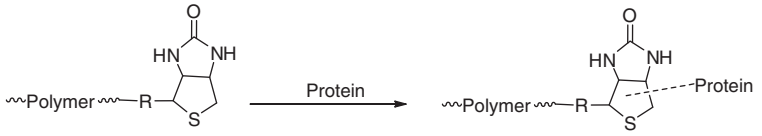
The process is mentioned under end-functional polymers. An example in the context of biopolymer conjugate formation is the coupling of alkyne end-functional poly(HEA), prepared by



Scheme 21. The aminooxy-ketone/aldehyde reaction.



Scheme 22. The azide-alkyne click reaction.



Scheme 23. Use of ligands that show specific protein binding.

Table 21. Multi-block polymers formed by interconnection of telechelics

Polymer 1 Monomer	RAFT agent	Polymer 2	Interconnection process	Ref.
HPMAm	**118**	Oligopeptide	Azide-alkyne click	[379]
HPMAm	**22**	Oligopeptide	Azide-alkyne click	[255]
HPMAm	**68**	Oligopeptide	Thiol-ene	[307]
MA, NIPAm	**26**, **27**	–	Thiobromo click	[241]

RAFT polymerization using trithiocarbonate (**161**), with an azide functional peptide.[448]

g) Attachment of Ligands that Show Specific Protein Binding (Scheme 23)

An example is that of biotin with streptavidin. RAFT agents containing a biotin moiety include **166** and **167**.[454] This chemistry was also exploited in preparing a heterotelechelic conjugate from α-glutathione-ω-biotin-poly(NIPAm).[450]

Most of the approaches (a–g above) have also been used in making (non-biopolymer) block, star, and graft copolymers.

Multiblock Copolymers

Multiblock copolymers are linear polymers consisting of more than three covalently interconnected polymer segments based on two or more different polymers or copolymer segments. The synthesis of multiblock copolymers has been performed by three different strategies.

The more traditional approach involves the interconnection of preformed telechelic polymers with suitably reactive end-groups which can be 'clicked' together to form the multiblock (Table 21). In this context, several papers have appeared on the synthesis of biodegradable HPMAm multiblocks.[255,307,379]

A second strategy relies simply on sequential monomer addition. Hadjiantoniou et al.[622] synthesized a series of block copolymers from di- through to a pentablock comprising poly (DMAEMA) and poly(MMA) segments by sequential addition starting with poly(DMAEMA)-dithiobenzoate prepared with cumyl dithiobenzoate. A series of blocks (diblock through tetrablock) with azide end-groups were synthesized and used for modifying silica particles.[429]

The third strategy employs either multi-RAFT agents or cyclic RAFT (when multi-RAFT agents are formed in situ). New reports on multi-block synthesis using such RAFT agents are included in Table 22. Ebeling and Vana[604] prepared multi-block copolymers based on the multi-trithiocarbonate **441**. Ebeling et al.[623] have also performed numerical simulations to predict the ideal molar mass distribution that should result from polymerizations using such agents.

Star Polymers

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

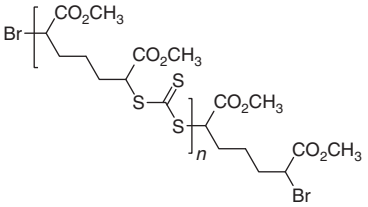
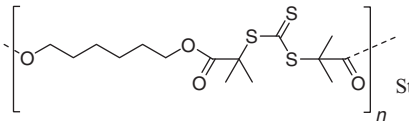
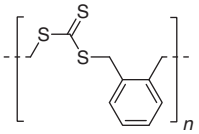
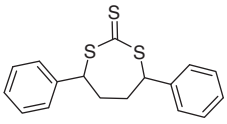
Multi-RAFT Agents

The multi-RAFT agent may in principle be a small organic compound, an organometallic complex, a dendrimer, a hyper-branched species, a macromolecular species, a particle or indeed any moiety possessing multiple thiocarbonylthio groups. Of these, macromolecular species and particles are considered in the section on *Polymer Brushes* below. Recent examples of star cores are shown in Table 4 (dithioesters), Table 8 (trithiocarbonates), and Table 10 (xanthates).

The first publications in this field[16] recognized two limiting forms of star (or graft/brush copolymer) growth depending on the orientation of the thiocarbonylthio group with respect to the core.

- In the first strategy, the propagating radicals are linear chains that dissociate from the core. 'Z'-connected RAFT agents (**445**, Scheme 24) are employed. The advantage of this strategy is that by-products from star–star coupling are unlikely. The thiocarbonylthio functionality is retained at the core of the star. A potential disadvantage of the 'propagation away from core' strategy is that reactions that cleave the thiocarbonylthio groups (e.g. aminolysis, thermolysis) cause destruction of the star structure (i.e. loss of the arms, Scheme 24). This feature can also be used to advantage in developing supported polymer syntheses or degradable network polymers (see *Polymer Networks*). A further potential issue is that the thiocarbonylthio functionality may become sterically inaccessible as polymerization proceeds.
- In the second strategy most propagating radicals remain attached to the core and 'R'-connected RAFT agents (**446**, Scheme 25) are used. Most thiocarbonylthio functionality remains on the periphery of the star. However, a linear macro-RAFT agent is released to the polymerization medium by the RAFT process. Since propagating radicals are attached to the core, termination by star–star coupling is a complication. Because the thiocarbonylthio groups are end-groups, they can be cleaved (e.g. by aminolysis) without destroying the star structure (Scheme 25).

Table 22. Polymerizations with multi- and cyclic RAFT agents

RAFT agent	Polymerization[A,B]
Multi-RAFT agent	
456 (Scheme 32)	(St)[603] MMA[603]
 **441**[604]	BA[604] St[604]
 **442**[624]	St[624] St-*b*-tBuSt[624]
 **443***[586]	DMAm/**408**[586] DMAm/**408**-*b*-NIPAm[586]
Cyclic RAFT agent	
 **444***	MA[563] tBA tBA-*b*-NIPAm[597]

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

The advantages and disadvantages of the two approaches are considered in detail in several papers and it is clear that the relative importance of the various factors mentioned above depends strongly on the particular monomer and RAFT agent used.

Luo et al.[625] have described the preparation of poly (NIPAm) 'stars' from a hyperbranched poly(glycidol) (HPG)-based macro-RAFT agent prepared as shown in Scheme 26.

Self-Condensing Vinyl Polymerization

A method for forming hyperbranched polymers by RAFT involves self-condensing vinyl polymerization. This involves copolymerization of monomers containing RAFT functionality. Examples of such RAFT inimers are **20**,[253] **23**,[460] **178**,[460] and **230**.[512] Star polymers can be formed by chain extension of the hyperbranched structure. The synthesis of St and acrylic polymers was achieved using dithiobenzoates, **20**[253] or **23**,[256] or trithiocarbonate, **178**,[460] and VAc polymers using xanthate, **230**.[512]

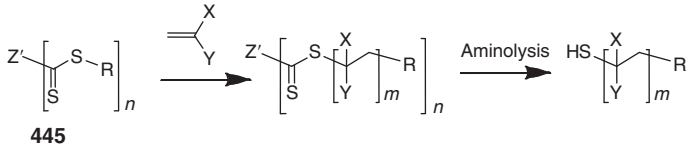
'Grafting to'

Various combinations of RAFT, ATRP, click, ring opening polymerization, and other methods have been used to synthesize star polymers, including mikto-arm stars.

Microgels and Nanoparticles

In this section we consider formation of polymer microgels, stars, or nanoparticles either by self-assembly and crosslinking of RAFT-synthesized block copolymers (Table 23) or by RAFT-mediated radical crosslinking polymerization (Table 24).

The work of the McCormick group in the area of nanoparticle formation by block copolymer self assembly and crosslinking and in using the structures formed as drug delivery vehicles has been reviewed.[47,53] The temperature-responsive triblock copolymer, PEO-*b*-poly(APMAm)-*b*-poly(NIPAm), was synthesized by RAFT polymerization in aqueous medium.[380] At room temperature, the polymer is hydrophilic and exists as unimers in aqueous solution. Increasing the solution temperature above the lower critical solution temperature (LCST) of the



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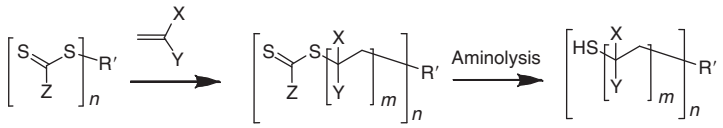
Scheme 24. Star polymer synthesis by the 'propagation away from core' strategy using a 'Z'-connected RAFT agent.



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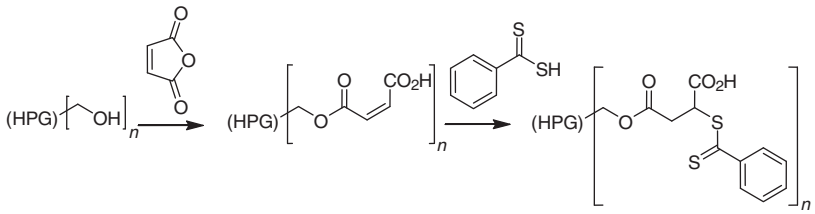
Scheme 25. Star polymer synthesis by the 'propagation attached to core' strategy using a 'R'-connected RAFT agent.



Scheme 26. Preparation of hyperbranched poly(glycidol) (HPG)-based macro-RAFT agent.[625]

Table 23. Recent examples of synthesis of microgels by block copolymer self assembly and crosslinking

Block copolymer[A]	Crosslinking process	Ref.
PEO-*b*-APMAm-*b*-NIPAm	Dialdehyde crosslinking of APMAm NH_2[B]	[380]
PEO-*b*-APMAm-*b*-**358**	Crosslinking of APMAm NH_2 with **447**[C]	[582]
DMEAEMA-*b*-NIPAm	Crosslinking with Au nanoparticles	[359]
DMAm/**296**-*b*-NIPAm/**296**	Photo-crosslinking of coumarin groups	[390]
396-*b*-PEGMA	Crosslinking with azide-alkyne click reaction	[167]
DMAm-*b*-**370**-*b*-**365**	Ionic crosslinking on change in pH	[383]

[A]See footnote B of Table 3.
[B]See Scheme 27 for details.
[C]See Chart 5 for structure.

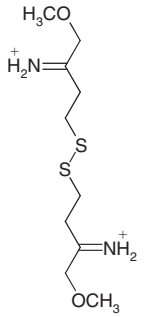


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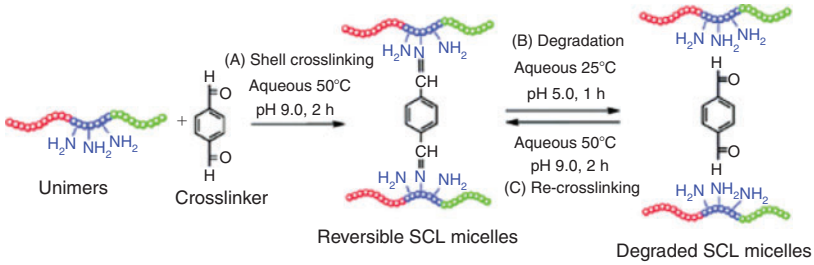
Chart 5.

poly(NIPAm) block leads to self-assembly into micelles with poly(NIPAm) in the core. The amine functionality of the poly (APMAm) shell was crosslinked with terephthaldicarboxaldehyde (TDA) at pH 9.0 to generate shell crosslinked micelles with

Table 24. Recent examples of synthesis of microgels and core-crosslinked star polymers by RAFT-mediated radical crosslinking polymerization

Arm monomer[A,B]	RAFT agent[C]	Monomer(s)[D]	Crosslinker[D]	Ref.
—	**115**	DEGMA/ PEGMA	EGDMA	[377]
PEGMA	**18**	—	**422**	[588]
PEGMA	**18**	—	**421**	[588]
PEGMA	**18**	—	DEGDMA	[588]
PEGMA	**97**	*BA*	*TEGMA*	[355]
PEGMA	**97**	*BA*	*MBAm*	[355]
DMAm	**173**	*BA*	*TEGMA*	[355]
DMAm	**173**	*BA*	*MBAm*	[355]
DMAm	**132**	*DEAm*	*MBAm*	[571]
PEGMA-*b*-EGMA	**173**	*BA*	*TEGMA*	[355]
PEGMA	**97**	*EGMA*	*TEGMA*	[353]
NIPAm	**138**	St	DVB	[419]
—	**158**	**397**	EGDMA	[584]
—	**158**	—	DVB	[626]
MA	**158**	—	DVB	[626]
—	**23**	DMAEMA	**422**	[256]
354	**145**	*St*	*423*	[427]
PFPA	**179**	—	MBAm	[463]
PFPA	**179**	—	**425**	[463]
PFPA	**179**	—	**424**	[463]
PEGA	**179**	VBA	MBAm	[462]
PEGA	**179**	VBA	**424**	[462]
PEGA	**179**	—	MBAm	[461]
PEGA	**179**	—	**425**	[461]
PEGA	**179**	—	**424**	[461]
PEGA	**179**	—	**426**	[461]
tBA	**179**	—	**424**	[461]
NIPAm	**179**	—	**424**	[461]

[A]See footnote B of Table 3.
[B]Monomer used in forming (linear) macro-RAFT agent when used.
[C]Initial RAFT agent used in synthesis of arm macro-RAFT agent.
[D]Monomer(s)/crosslinker (refer to Fig. 16) used in radical crosslinking polymerization.



Scheme 27. Self assembly and reversible crosslinking of PEO-*b*-poly(APMAm)-*b*-poly(NIPAm). Scheme reproduced from Ref. [380], copyright American Chemical Society.

cleavable imine linkages (Scheme 27). The material has potential application in pH triggered drug delivery.

One of the more popular methods for forming both microgels (nanogels) and core-crosslinked star polymers involves (co)polymerization of a divinyl-monomer using RAFT or another form of RDRP. Star polymers can be formed either through use of a linear macro-RAFT agent in initial microgel formation or by use of an initially formed microgel as a macro-RAFT agent in a subsequent RAFT polymerization. These approaches can be combined to form mikto-arm stars.

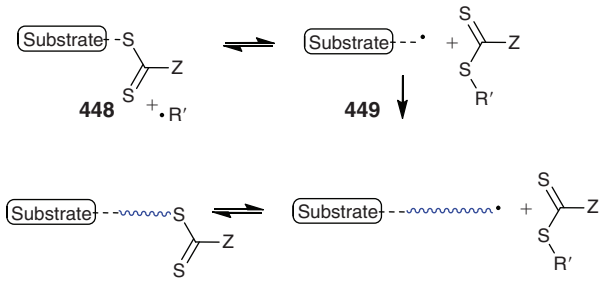
Examples of applying these strategies are included in Table 24. The conditions for the synthesis of well defined, low dispersity, 'arm-first' star copolymers based on poly(PEGA), poly(NIPAm), and poly(tBuA) have been explored. For systems which generate poorly soluble crosslinked cores, an efficient (close to quantitative) incorporation of arms into the star polymer structure and a low dispersity product was observed. In contrast, with a solvent compatible crosslinked core, the extent of incorporation of the arms was significantly reduced and molecular weight distributions were broader.

Lubrizol have undertaken the large scale commercialization of RAFT-mediated radical crosslinking polymerization in producing a star polymer rheology control agent for oil.[160]

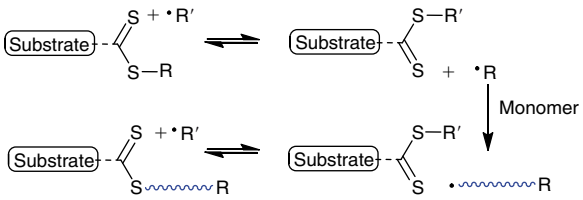
Metal Nanoparticles

A wide variety of processes have been exploited with a view to preparing gold and other metal nanoparticles. A summary of the literature through to 2007 is contained in our recent review.[62] Some recent examples are as follows:

- Azide functional gold nanoparticles were reacted with RAFT-synthesized alkyne-functional poly(4VP)[388] or poly(CMS)-*b*-poly(St).[447]
- Core crosslinked micelles were formed from poly(MPC)-*b*-poly(DMAEMA/NIPAm) and $HAuCl_4 \cdot 4H_2O$.[426]
- Polymers (including poly(tBA) and poly(NIPAm)) prepared with trithiocarbonate **159** were used to coat gold nanoparticles.[445]
- Diblock copolymer, poly(NIPAm)-*b*-poly(DMAEAm)[367] and PEGA[349] with trithiocarbonate ends were used to form colloidally stable gold nanoparticles.
- Diblock copolymer poly(BA)-*b*-poly(NIPAm) with xanthate ends and a derived thiol were used to form colloidally stable gold nanoparticles.[112]
- Thiol terminated methacrylamide polymers were prepared by post RAFT polymerization modification of poly (PFPMA).[226] These were used to form a library of gold nanoparticles.



Scheme 28. 'Grafting from' with 'R' connected RAFT agent.



Scheme 29. 'Grafting from' with 'Z' connected RAFT agent.

Scheme 30. First step in 'grafting through'.

- Thiol terminated poly(St) grafted Fe_3O_4 nanoparticles were used in forming gold nanoparticles.[407]
- End-groups of poly(St) prepared with **89**,[338] poly(NIPAm) prepared with **251**,[536] and poly(NVCL) prepared with **227**[505] were functionalized with thio end-groups and these polymers were used in forming gold nanoparticles.
- Single chain nanoparticles formed by photo-crosslinking of poly(DMAEMA/**296**) were used as nanoreactors in forming gold nanoparticles.[197]

Polymer Brushes/Graft Copolymers/Comb Polymers/ Surface Modification

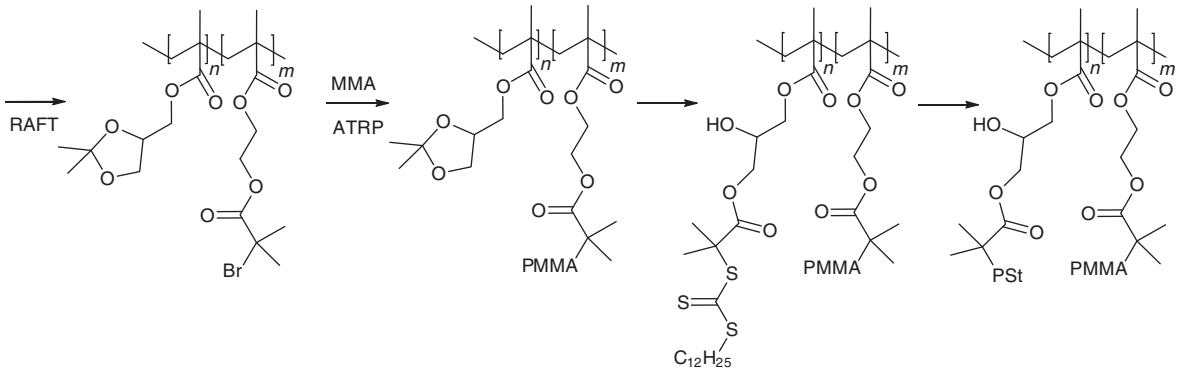
There have been several recent reviews on surface modification. Four approaches will be considered with reference to polymer surface modification.[627]

- The 'grafting from' process making use of substrates where 'R' is bound to the surface (Scheme 28). It is possible to form such 'R' connected RAFT agents (**448**) directly and use these in 'grafting from'. It is also possible

Table 25. Macro-RAFT agents used in RAFT graft copolymerization

Substrate	RAFT agent[A]	Polymerization[B]	Comments
'R-attached'			
Hyperbranched poly(glycidol)	Scheme 26	NIPAm[625]	
BSA	**139**	NIPAm[420] NIPAm-*b*-DMAm[420]	Thiol-ene
Cellulose	**156**	EA[629] NIPAm[629]	DCC/DMAP
PLA			
Poly(MMA-*co*-TMSEMA)	**136**	NIPAm[630]	Alkyne-azide 'click'[C]
Poly(TMSEMA)	**226**	VAc[631]	DCC/DMAP[C]
Loprodyne (hydroxylated nylon-6,6 membrane)	**121**	NIPAm[382]	DIC/DMAP
Polypropylene	**89**	AA[632] AA-*b*-Am[632]	UV initiator grafted to surface, used in AA polymerization in presence of **89**. Am grafted
Divinylbenzene microspheres	**11**	**312**[166]	RAFT agent attached by single unit monomer insertion.
Fe_3O_4 nanoparticles	**130**	St[407]	Amine functional nanoparticles modified with **130**.
Gold/ITO surface	**30**	St[213] St-*b*-tBA[213]	[D]
Gold/ITO surface	**31**	MMA-*b*-St[263]	[D]
ITO surface	**32**	St[264]	[D]
'Z-attached'			
Soy protein	**181**	AA[466] Am[466]	Active ester-amine
poly(PSt/MAH) breath figure	**179**	NIPAm[464] NIPAm/**372**[464]	Acid chloride
Graphene oxide	**123**	NVC[633]	DCC/DMAP

[A]RAFT agent used to modify the surface.
[B]See footnote B of Table 3.
[C]Substrate polymer prepared by ATRP, TMSEMA units converted into HEMA units and OH groups esterified to provide RAFT agent functionality.
[D]RAFT agent electrodeposited on gold or ITO surface.



Scheme 31. Formation of block-bottle brush polymer by tandem ATRP-RAFT.[628]

to produce radicals on the surface (**449**) by irradiation, from attached initiator functionality, or by grafting through (Scheme 30) and thereby form the 'R' connected RAFT in situ during RAFT polymerization.

- The 'grafting from' process making use of substrates where 'Z' is bound to the surface (Scheme 29).
- The 'grafting through' which involves conducting a RAFT polymerization in the presence of a surface with monomer functionality (Scheme 30). The mechanism is then the same as shown in Scheme 28.
- The 'grafting to' process in which a RAFT-synthesized polymer is attached to the surface.

Grafting-from Processes

Macro-RAFT agents used as substrates in grafting from process have been included in Table 25.

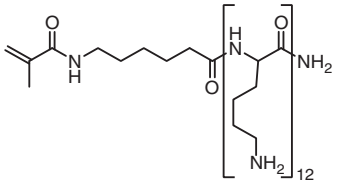
RAFT polymerization has also been used to prepare substrates for 'grafting from' by ATRP. The process involves copolymerization of monomer(s) containing ATRP initiator functionality (e.g. **416**[587] and **417**[203]). An example of this is shown in Scheme 31.[628]

Grafting-through Processes

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

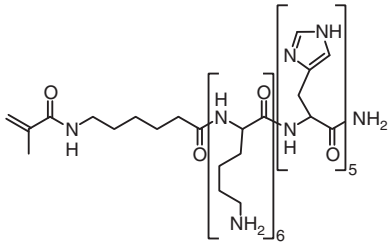
- A polymer chain (Fig. 19)
- Particles and surfaces. Nanocomposite materials have been prepared by grafting through polymerization. Examples include:
  - Grafting through polymerization of glycomonomers to divinylbenzene based polymer microspheres in the presence of cumyl dithiobenzoate.[166]

- Grafting through polymerization of MMA, St, and tBA with 2-((phenylcarbonothioyl)thio)acetic acid **61** as RAFT agent to gold or ITO surfaces functionalized with **454** by electrodeposition. The RAFT agent **61** is a poor RAFT agent and does not provide control over MMA polymerization, yet free poly(MMA) obtained under these conditions was reported to have a very narrow dispersity.[634]



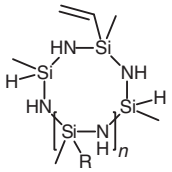
450

Peptide macromonomer[363]



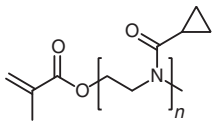
451

Peptide macromonomer[363]



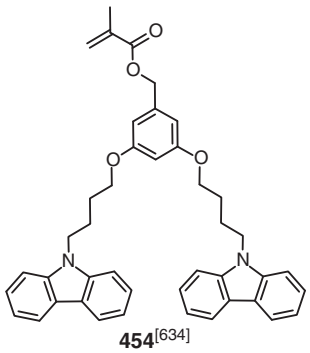
452

Vinylcyclosilazane, R = H or vinyl, n ~20[535]

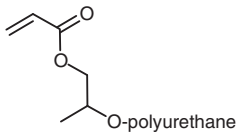


453

Poly(2-cyclopropyl-2-oxazoline) macromonomer[190]



454[634]



Polyurethane acrylate[635]

Fig. 19. Macromonomers subjected to RAFT polymerization.

The process of formation of polymers containing active ester functionality or pyridyl disulfide functionality as substrates for 'grafting to processes' (see above) might also be considered as examples of 'grafting through' processes.

Grafting-to Processes

One use of RAFT polymerization in the 'grafting-to' approach involves synthesis of polymers with reactive end-groups or block structures by RAFT polymerization which are then self-assembled and/or bonded to a particle, surface, or other structure.

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

Covalent attachment to graphene has the drawback that the bonds formed may disrupt the conjugated structure thereby leading to compromised physical or electronic properties. Thus, 'grafting to' approaches that involve non-covalent attachment based on π–π stacking seem attractive. Pyrene end-functional poly(NIPAm),[455] poly(DMAEA), and PAA[456] were prepared using a pyrene end-functional RAFT agent which was used in forming graphene composites.

RAFT-synthesized polymers based on trithiocarbonate **149** with trimethoxysilane functionality on Z were grafted to silica particles.[432] Since only the chains with the RAFT end-group were grafted, the process provides a method of polymer purification. The grafted chains were shown to be living through chain extension experiments and could be cleaved from the support by aminolysis.

Hou et al.[594] have reported on grafting RAFT-synthesized polymers to fused silica particles functionalized with 'Z'-connected RAFT agent by a radical exchange process. Degrafting was also accomplished by addition-fragmentation coupling. Further examples include:

- The use of azide-alkyne click chemistry in coupling poly(VAc) (formed with **231**) to azide-functional starch.[518]
- The use of thiol-ene chemistry to attach a glycopolymer to divinylbenzene microspheres.[166]
- RAFT-synthesized PAA (co)polymers as dispersants in preparing CdS quantum dot nanocomposites.[325]
- The use of the thiocarbonyl hetero-Diels Alder reaction to couple poly(iBA) (formed with **57**) to cyclopentadiene-functional cellulose.[295]

Polymer Networks

Polymer networks can be formed by crosslinking RAFT-synthesized homopolymers, block copolymers, or star polymers, or can be formed directly by a RAFT (co)polymerization in the presence of crosslinking monomer (e.g. a divinyl monomer such as EGDMA, MBAm, TEGDMA, DVB, or **418**–**425** (Fig. 16)). A wide variety of crosslinking processes have been explored. Polymer networks have been applied in controlled release applications (pharmaceuticals, agrochemicals) and as media for chromatography.[577,636]

Degradable Networks

A poly(AA/MMA) dithiobenzoate macro-RAFT agent was used in preparing an acid degradable pH responsive network with **455** (Chart 6) as crosslinking agent.[269]

Hydrogels

A PNVP xanthate macro-RAFT agent was used in preparing a PNIPAm hydrogel with MBAm as crosslinking agent.[491]

Porous Polymer Monoliths

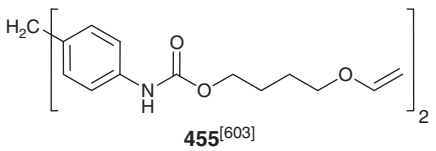
These were prepared:

- from MAA with EGDMA as crosslinker and dibenzyl trithiocarbonate (**89**) as RAFT agent.[636] The RAFT agent used is unlikely to provide good control over MAA polymerization. The monolith was formed in the presence of clenbuterol to provide molecular imprinting.
- from EHMA with EGDMA as crosslinker and dibenzyl trithiocarbonate (**89**) as RAFT agent.[577] The RAFT agent is unlikely to provide good control over EHMA polymerization. The monolith was formed in the presence of propan-1-ol/butane-1,4-diol as porogen. The monolith was further modified by surface RAFT polymerization of glycerol monomethacrylate (**289**).
- from RAFT-synthesized PLA-*b*-poly(St/**386**) crosslinked by metathesis polymerization.[413] Nanopores were formed by etching of PLA phase.

Molecular Imprinted Polymers

These were prepared (see also bullet one under monoliths above):

- from MAA with EGDMA as crosslinker and either benzyl dithiobenzoate (**54**) or benzyl dithioisobutyrate (**74**) as RAFT agent.[291] Neither RAFT agent is likely to provide good control over MAA polymerization. Particles were formed in the presence of atrazine, to provide molecular imprinting, and acetonitrile as porogen.
- from 4VP with EGDMA as crosslinker and cumyl dithiobenzoate (**11**) as RAFT agent.[177] Particles were formed in the presence of 2,4-dichlorophenoxyacetic acid, to provide molecular imprinting, and methanol/water as porogen.



455[603]

Chart 6.

Kinetics of Network Formation

A study of the kinetics of St/DVB copolymerization with *S*-thiobenzoyl thioglycolic acid (**61**) as RAFT agent and with BPO initiator at 80°C was carried out.[301] Delayed gelation, lower molecular weights pre-gelation, and higher degrees of swelling for the network prepared by RAFT polymerization were considered consistent with the molecular weight between crosslinks and the crosslink density being more homogeneous.

Methacrylic Networks

Addition of trithiocarbonate **79** was found to reduce the volumetric shrinkage stress in crosslinked multi(meth)acrylate networks without influence on the glass transition temperature.[322] The rate of polymerization was reduced compared with that for the similar polymerization in the absence of **79**.

RAFT Extensible Networks

The reaction of a thiomalic acid based polyester with thiocarbonyl-bis-imidazole provided a network with trithiocarbonate crosslinks (**456**, Scheme 32).[603] The crosslinks were then extended by RAFT polymerization of MMA or St. The poly(MMA) or poly(St) was cleaved from the network by aminolysis and characterized by GPC. This indicated moderate control over MMA polymerization ($Đ < 1.5$) but poor control over St polymerization ($Đ > 4$). The latter result may have been compromized by oxidative coupling of the α,ω-thiolo-poly(St) product.

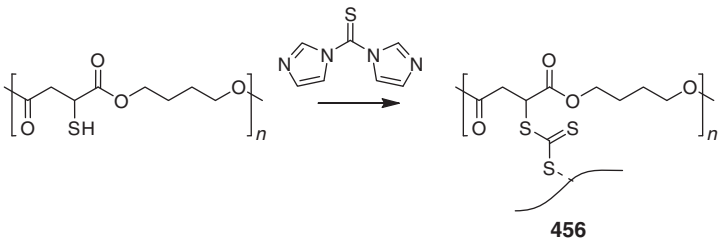
A gold nanoparticle network with trithiocarbonate crosslinks was formed from azide functional gold nanoparticles and the bis alkyne RAFT agent **82**. The crosslinks were then extended by RAFT polymerization of NIPAm.[332]

US Patents on RAFT

Table 26 provides a list of granted US patents published during 2009-early 2012 and is an update to the list that appeared in the *Encyclopedia of Polymer Science*.[551] The list includes three divisionals of the original CSIRO RAFT patent.[637–639]

Conclusions

The last two years has seen a further substantial expansion in the number of papers on applications of RAFT polymerization. These applications cover a diverse range of areas ranging from biomedical and optoelectronic applications to coatings and rheology control agents. This has meant a reduction in the number of papers that explore RAFT polymerization as a technique but rather an increase as people seek both to improve the process and further define the intimate details of the RAFT mechanism. We anticipate these trends will continue.



456

Scheme 32. Preparation of network with trithiocarbonate crosslinks.[603]

Table 26. Granted US patents pertaining to RAFT polymerization published between 2009 and early 2012

Number	Date[A]	Assignee	Title	Brief description
US 7 652 736[640]	2010	3M	Infrared light reflecting film	Acrylate polymer with liquid crystalline pendants made by RAFT polymerization with trithiocarbonate **123**.
US 8 110 626[641]	2012	Advanced Polymerik	Dispersing agents in composites	Dispersants as in US 7 837 899 for talc (and other particles) in polymers.
US 7 837 899[642]	2010	Polymers Australia	Dispersing agents in nanocomposites	Copolymer dispersants prepared by controlled radical polymerization (ATRP, RAFT, NMP) for clay in polymer nanocomposites.
US 7 674 843[643]	2010	Agfa Graphics	Stable pigment dispersions	Dispersions containing RAFT synthesized dispersants.
US 7 678 845[644]	2010	Agfa Graphics	Stable pigment dispersions	Dispersions containing RAFT synthesized dispersants.
US 7 691 937[645]	2010	Agfa Graphics	Polymeric dispersants containing (meth)acryloyloxybenzoic acid	RAFT synthesized pigment dispersant block copolymers.
US 7 713 508[646]	2010	Arrowhead Center	Thiation of carbon nanotubes and composite formation	RAFT agents on carbon nanotubes.
US 8 133 960[647]	2012	Bausch & Lomb	Biomedical devices	Biomedical devices.
US 8 100 528[648]	2012	Bausch & Lomb	Coating solutions comprising segmented interactive block copolymers	Block copolymers made by RAFT
US 8 083 348[649]	2011	Bausch & Lomb	Biomedical devices	Contact lenses.
US 8 043 369[650]	2011	Bausch & Lomb	Biomedical devices	Silicone hydrogels.
US 7 942 929[651]	2011	Bausch & Lomb	Coating solutions comprising segmented reactive block copolymers	Surface treatment.
US 8 133 411[652]	2012	Biomerieux SA, CNRS	Fluorescent polymers soluble in an aqueous solution and a method for the production thereof	Fluorescent RAFT-synthesized polymer in medical diagnostics or therapeutics.
US 7 517 914[653]	2009	Boston Scientific	Controlled degradation materials for therapeutic agent delivery	Controlled release of therapeutics.
US 7 851 544[654]	2010	Byk-Chemie	Copolymers containing three segments of different ion density, method for their production and application of the same	Triblock copolymers made by RAFT used as pigment dispersants.
US 7 795 355[655]	2010	Carnegie Mellon University	Preparation of functional polymers	RDRP-click. Includes RAFT examples.
US 8 110 130[656]	2012	Coatex SAS	Use of a rheological additive in the manufacture by vibrocompaction of a water and hydraulic binder based formulation, formulation obtained	Additive made by RAFT.
US 8 053 497[657]	2011	Coatex SAS	Polymers produced by using sulfur compounds in the form of transfer agents for controlled radical polymerization of acrylic acid and the use thereof	Poly(AA) by RAFT polymerization in water.
US 7 956 211[658]	2011	Coatex SAS	Trithiocarbonate derivatives and the use thereof in the form of transfer agents for acrylic acid controlled radical polymerization	Trithiocarbonates used for RAFT AA polymerization in water.
US 7 851 572[659]	2010	Coatex SAS	Polymers produced by using sulfur compounds in the form of transfer agents for controlled radical polymerization of acrylic acid and the use thereof	Low dispersity AA copolymers by RAFT polymerization.
US 7 960 479[660]	2011	Conopco, Inc.	Brush copolymers	Brush copolymers made by ROMP/RAFT.
US 7 811 555[661]	2010	Cordis Corporation	Tri-branched biologically active copolymer	Tri-branched copolymers. Biomedical applications.

(*Continued*)

Table 26. (Continued)

Number	Date[A]	Assignee	Title	Brief description
US 8 124 188[662]	2012	CSIRO	Polymeric coatings and methods for forming them	Surface initiated polymerization.
US 7 666 962[637]	2010	CSIRO	Polymerization With Living Characteristics	Original RAFT Patent. (polymers)
US 7 662 986[638]	2010	CSIRO	Polymerization With Living Characteristics	Original RAFT Patent. (chain transfer agents)
US 7 714 075[639]	2010	CSIRO	Polymerization With Living Characteristics	Original RAFT Patent. (block copolymers)
US 7 807 755[663]	2010	CSIRO	Method for removing sulfur-containing end-groups	End-group removal with hypophosphite.
US 7 696 292[664]	2010	DuPont	Low-polydispersity photoimageable acrylic polymers, photoresists and processes for microlithography	Resist polymers made by RAFT.
US 8 034 534[665]	2011	DuPont	Fluorinated polymers for use in immersion lithography	Resist polymers made by RAFT.
US 7 632 966[666]	2009	DuPont	Synthesis of trithiocarbonate RAFT agents and intermediates thereof	RAFT agent synthesis.
US 8 142 977[667]	2012	Fujifilm	Positive resist composition and pattern forming method using the same	RAFT is indicated as a preferred method for polymers synthesis.
US 8 178 637[668]	2012	Goodyear	Controlled Polymerization	Preparation of poly(St)-*b*-(diene-*co*-AN) by RAFT and other RDRP in emulsion.
US 7 812 108[669]	2010	Goodyear	Hydrogenation and epoxidation of polymers made by controlled polymerization	Hydrogenation of RAFT-synthesized polymers with hydrazine.
US 7 671 152[670]	2010	Goodyear	Surfactantless synthesis of amphiphilic cationic block copolymers	Poly(4VP) macro-RAFT agent derived block copolymers.
US 7 767 775[671]	2010	Goodyear	Controlled Polymerization	Preparation of poly(St)-*b*-(diene-*co*-MAN) and other MAN blocks by RAFT emulsion polymerization.
US 7 625 985[672]	2009	Goodyear	Water-based process for the preparation of polymer-clay nanocomposites	Poly(4VP) block copolymers used in water as dispersants/exfoliants for clay nanocomposites.
US 7 592 409[673]	2009	Goodyear	Styrene acrylonitrile isoprene triblock copolymer	Triblock made by RAFT emulsion polymerization.
US 7 528 204[674]	2009	Goodyear	Hydrogenation and epoxidation of polymers made by controlled polymerization	RAFT emulsion polymerization followed by other processes.
US 7 989 026[675]	2011	IBM	Method of use of epoxy-containing cycloaliphatic acrylic polymers as orientation control layers for block copolymer thin films	Poly(St)-*b*-poly(MMA) used in process was made by RAFT.
US 7 763 319[676]	2010	IBM	Method of controlling orientation of domains in block copolymer films	Poly(St)-*b*-poly(MMA) used but no explicit mention of RAFT in the examples.
US 7 521 094[677]	2009	IBM	Method of forming polymer features by directed self-assembly of block copolymers	Poly(St)-*b*-poly(MMA) used in process was made by RAFT.
US 7 521 090[678]	2009	IBM	Method of use of epoxy-containing cycloaliphatic acrylic polymers as orientation control layers for block copolymer thin films	Poly(St)-*b*-poly(MMA) used in process was made by RAFT.
US 7 612 153[679]	2009	Intezyne Technologies, Inc.,	Heterobifunctional poly(ethylene glycol) and uses thereof	Includes synthesis of PEG based RAFT agents
US 7 968 743[680]	2011	ITRI, Taiwan	Thiocarbonylthio compound and free radical polymerization employing the same	RAFT agents with R = sulfonylmethyl or with Z = CF_3
US 7 799 568[681]	2010	Johns Hopkins University	Authentication of products using molecularly imprinted polymers	Molecularly imprinted polymers.
US 7 678 870[682]	2010	Johns Hopkins University	Processable molecularly imprinted polymers	Molecularly imprinted polymers.

(*Continued*)

Table 26. (Continued)

Number	Date[A]	Assignee	Title	Brief description
US 7 510 817[683]	2009	JSR	Photoresist polymer compositions	Photoresists based on bulky methacrylates.
US 7 517 634[684]	2009	JSR	Photoresist polymers	Photoresists based on bulky methacrylates.
US 7 875 213[685]	2011	Kemira Oyj	Mineral dispersants and methods for preparing mineral slurries using the same	RAFT made dispersants based on trithiocarbonates.
US 7 825 193[686]	2010	Lanxess	Dithiocarbamic esters	RAFT agents Z = nitrogen heterocycle and R = haloalkenyl and use in chloroprene polymerization.
US 7 951 888[687]	2011	L'Oreal	Block copolymer, composition comprising it and cosmetic treatment process	Block copolymers for cosmetic or pharmaceutical compositions.
US 7 816 464[688]	2010	L'Oreal	Polymer particle dispersion, cosmetic composition comprising it and cosmetic process using it	RAFT synthesized blocks for dispersion of polymer particles in a liquid silicone medium.
US 7 632 905[689]	2009	L'Oreal	Block copolymer, composition comprising it and cosmetic treatment process	Block copolymer composition for use in cosmetics.
US 7 585 922[690]	2009	L'Oreal	Polymer particle dispersion, cosmetic compositions comprising it and cosmetic process using it	Block copolymers containing a segment based on methacrylates with silane functionality made by RAFT.
US 8 137 754[691]	2012	Lubrizol	Hydroxyl-terminated thiocarbonate containing compounds, polymers, and copolymers, and polyurethanes and urethane acrylics made therefrom	Synthesis of hydroxyl-functional telechelics for use in polyurethanes.
US 8 012 917[692]	2011	Lubrizol	Crosslinked polymer	Star microgel oil additives.
US 7 851 582[693]	2010	Lubrizol	S-(α, α′-disubstituted-α″-acetic acid)–substituted dithiocarbonate derivatives for controlled radical polymerizations, process and polymers made therefrom	Xanthate RAFT agents.
US 7 659 345[694]	2010	Lubrizol	S,S′-bis-(α, α′-Disubstituted-α″-Acetic acid)–trithiocarbonates and derivatives as initiator–chain transfer agent–terminator for controlled radical polymerizations and the process for making the same	Polymer composition claim.
US 7 495 128[695]	2009	Lubrizol	S-S′-bis-(α, α′-Disubstituted-α″-acetic acid)–trithiocarbonates and derivatives as initiator–chain transfer agent–terminator for controlled radical polymerizations and the process for making the same	Trithiocarbonate RAFT agents.
US 7 495 050[696]	2009	Lubrizol	Associative thickeners for aqueous systems	Rheology modifiers prepared by RAFT.
US 7 498 456[697]	2009	Lubrizol	S-(α, α′-disubstituted-α″-acetic acid) substituted dithiocarbonate derivatives for controlled radical polymerization, process and polymers made therefrom	Synthesis and use of xanthate RAFT agents.
US 7 789 160[698]	2010	Rhodia	Addition of non-ionic surfactants to water soluble block copolymers to increase the stability of the copolymer in aqueous solutions containing salt and/or surfactants	Amphiphilic block copolymers for oil recovery applications.

(*Continued*)

Table 26. (Continued)

Number	Date[A]	Assignee	Title	Brief description
US 7 473 740[699]	2009	Rhodia	Method for partial or total oxidation of one or several thiocarbonylthio ends of a polymer obtained by radical polymerization controlled by reversible addition-fragmentation	Ozonolysis of RAFT end-groups.
US 7 473 730[700]	2009	Rhodia	Method for depositing a polymer onto a surface by applying a composition onto said surface	Block copolymer containing ionic block for cosmetic applications.
US 7 531 597[701]	2009	Rhodia	Formulation comprising an ionic compound, a polyionic polymer, and a block copolymer	Block copolymer containing ionic block for cosmetic applications. Formulation for stable dispersion.
US 7 659 350[702]	2010	Princeton University	Polymerization method for formation of thermally exfoliated graphite oxide containing polymer	Grafting to oxidized graphite. Nanocomposites with carbon nanotubes.
US 7 498 398[703]	2009	SABIC Innovative Plastics	Thermoplastic composition, method of making, and articles formed therefrom	Polycarbonates including acrylate blocks.
US 8 129 470[704]	2012	Tesa	Adhesive masses based on block copolymers of structure P(A)–P(B)–P(A) and P(B)–P(A)–P(B)	Triblock polymers made by RAFT in adhesive compositions.
US 8 012 581[705]	2011	Tesa	Bilayer pressure-sensitive adhesives	Adhesives made by RAFT.
US 7 758 933[706]	2010	Tesa	Adhesive materials having a high refractive index based on acrylate block copolymers	Pressure-sensitive adhesive comprising an acrylate block copolymer with high refractive index.
US 7 605 212[707]	2009	Tesa	Method for producing contact adhesive masses containing acrylic	Contact adhesives made by RAFT. Dibenzyl trithiocarbonate used.
US 7 514 515[708]	2009	Tesa	Method for the production of acrylate adhesive materials using metal-sulfur compounds	Pressure sensitive adhesives. Contains metal complexes.
US 7 521 487[709]	2009	Tesa	Pressure-sensitive adhesive with dual crosslinking mechanism	Acrylic pressure sensitive adhesives. Benzyl dithiobenzoate used.
US 8 153 729[710]	2012	University of California, Mitsubishi Chemical	Highly efficient agents for dispersion of nanoparticles in matrix materials	RAFT-synthesized hyperbranched polymers as dispersants.
US 7 943 680[711]	2011	University of Colorado	Stress relaxation in crosslinked polymers	Use of a RAFT process to control stress in crosslinking polymerization.
US 7 687 600[712]	2010	University of Massachusetts	Invertible amphiphilic polymers	Invertible micelles for drug delivery from block copolymers made by RAFT.
US 7 999 020[713]	2011	University of Minnesota	Ion gels and electronic devices utilizing ion gels	An ion-gel including an ionic liquid and a block copolymer.
US 8 084 558[714]	2011	University of Southern Mississippi	Preparation of transition metal nanoparticles and surfaces modified with (co)polymers synthesized by RAFT	Transition metal nanoparticles and surfaces.
US 7 718 432[715]	2010	University of Southern Mississippi	Non-immunogenic, hydrophilic/cationic block copolymers and uses thereof	HPMAm block copolymer for controlled release applications.
US 7 745 553[716]	2010	University of Sydney	Aqueous dispersions of polymer particles	RAFT in emulsion.
US 7 981 688[717]	2011	University of Washington	Stimuli-responsive magnetic nanoparticles and related methods	Stimuli-responsive magnetic nanoparticles.
US 7 718 193[718]	2010	University of Washington	Temperature- and pH-responsive polymer compositions	Block copolymers.
US 7 935 782[719]	2011	Vanderbilt University	Multifunctional degradable nanoparticles with control over size and functionalities	Drug delivery based on crosslinked nanoparticles made by RAFT.
US 8 147 985[720]	2012	None	Diamond coating by living polymerization	Process for surface modification with chromatographic applications.

[A]Date of publication.

Abbreviations

AcS 4-acetoxystyrene
AA acrylic acid
AAEMA 2-(acetoacetoxy)ethyl methacrylate
AEMA 2-aminoethyl methacrylate (hydrochloride)
AEMAm *N*-(2-aminoethyl)methacrylamide (hydrochloride)
AEP 2-(acryloyloxy)ethyl phosphate
AIBN azoisobutyronitrile
ACHN azobis(1-cyclohexanenitrile)
ACVA azobis(cyanovaleric acid)
Am acrylamide
AMA allyl methacrylate
AMPS 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS)
AN acrylonitrile
APMAm *N*-(3-aminopropyl)methacrylamide (hydrochloride)
ATRP atom transfer radical polymerization
BA butyl acrylate
BAm *N*-butylacrylamide
BD butadiene
BES 1-butyl ethenesulfonate
BMA butyl methacrylate
BzAm *N*-benzylacrylamide
BDSMA *t*-butyldimethylsilyl methacrylate
BP β-pinene
ClPEA 2-chloropropionyloxyethyl acrylate
BPO dibenzoyl peroxide
CHAm *N*-cyclohexylacrylamide
CCT catalytic chain transfer
CHMA cycylohexyl methacrylate
CMS 4-(chloromethyl)styrene
CMA cholesteryl methacrylate
CPA 3-chloropropyl acrylate
$Đ$ molar mass dispersity = ratio of mass average to number average molar mass[721]
DA dodecyl acrylate
DAAm diacetone acrylamide (*N*-(1,1-dimethyl-3-oxobutyl) acrylamide)
DADMAC diallyldimethylammonium chloride
Dc 1-decene
DEAm *N,N*-diethylacrylamide
DEAEMA 2-(diethylamino)ethyl methacrylate
DEAPMAm *N*-(3-(diethylamino)propyl)methacrylamide (hydrochloride)
DEGDMA diethyleneglycol dimethacrylate
DEGMA (diethylene glycol monomethyl ether) methacrylate
DEHEA di(ethylene glycol) 2-ethylhexyl ether acrylate
DFHA decafluoroheptyl acrylate
DMAm *N,N*-dimethylacrylamide
DMAEA 2-(dimethylamino)ethyl acrylate
DMAEAm *N*-(2-(dimethylamino)ethyl)acrylamide
DMAEMA 2-(dimethylamino)ethyl methacrylate
DMAPMAm *N*-(3-(dimethylamino)propyl)methacrylamide (hydrochloride)
DPAEMA 2-(diisopropylamino)ethyl methacrylate
DVB divinylbenzene
EA ethyl acrylate
EAA ethyl α-acetoxyacrylate
E ethene
EEA ethoxyethyl acrylate
EGDMA ethyleneglycol dimethacrylate
EGMA (ethylene glycol monomethyl ether) methacrylate
EHA 2-ethylhexyl acrylate
EVC *N*-ethyl-3-vinylcarbazole
EVE ethyl vinyl ether
GMA glycidyl methacrylate
HA hexyl acrylate
HDDA hexane-1,6-diol diacrylate
HEA 2-hydroxyethyl acrylate
HEAm 2-hydroxyethylacylamide
HEMA 2-hydroxyethyl methacrylate
HMA hexylmethacrylate
HMS 4-(hydroxymethyl)styrene
HPMA 2-hydroxypropyl methacrylate
HPMAm *N*-2-hydroxypropyl methacrylamide
iBoA isobornyl acrylate
iBMA isobutyl methacrylate
Ip isoprene
IPhMA 4-iodophenyl methacrylate
iPOx 2-isopropenyl-2-oxazoline
IUPAC International Union of Pure and Applied Chemistry
LAM less activated monomers (includes vinyl monomers such as VAc, NVP and NVC)
Lim limonene
LMA dodecyl methacrylate
LPO didodecanoyl peroxide (dilauroyl peroxide)
MA methyl acrylate
MADIX macromolecular design by interchange of xanthate
MAEP 2-(methacryloyloxy)ethyl phosphate
MAH maleic anhydride
MAM more activated monomers (includes styrenes, acrylates, and acrylamides)
MAN methacrylonitrile
MBAm methylene-bis-acrylamide
MMA methyl methacrylate
MMBL γ-methyl-α-methylene-χ-butyrolactone
MPC methacryloyloxyethyl phosphorylcholine
MVK methyl vinyl ketone
NAPM *N*-acryloyl-L-proline methyl ester
NAPAM *N*-acryloyl-L-phenylalanine methyl ester
NAP *N*-acryloylpyrrolidine
NAS *N*-acryloyloxysuccinimide
NEMI *N*-ethylmaleimide
NES neopentyl ethenesulfonate
NIPAm *N*-isopropylacrylamide
NMMI *N*-methylmaleimide
NMP aminoxyl-(nitroxide-)mediated polymerization
NPMI *N*-phenylmaleimide
NMS *N*-methacryloyloxysuccinimide
NVC *N*-vinylcarbazole
NVCL *N*-vinylcaprolactam
NVP *N*-vinylpyrrolidone
NVPI *N*-vinylphthalimide
SMe 4-methylstyrene
OAm *N*-octylacrylamide
PAm *N*-propylacrylamide
PA propargyl acrylate
PAA α-propylacrylic acid (2-methylenepentanoic acid)
PCL poly(caprolactone)
PDMS poly(dimethylsiloxane)
PE polyethylene
PEG poly(ethylene glycol) monomethyl ether
PEGA (poly(ethylene glycol) monomethyl ether) acrylate
PEGMA (poly(ethylene glycol) monomethyl ether) methacrylate

PEO poly(ethylene oxide)
PFPMA pentafluorophenyl methacrylate
PFPVB pentafluorophenyl 4-vinylbenzoate
PFPVS pentafluorophenyl 4-vinylbenzenesulfonate
PFS pentafluorostyrene
PLA poly(lactic acid)
PMA propargyl methacrylate
PMVE perfluoro(methyl vinyl ether)
POSS isobutyl polyhedral oligomeric silsesquioxane
PVK phenyl vinyl ketone
PVS phenyl 4-vinylbenzenesulfonate
py pyridine
RAFT reversible addition–fragmentation chain transfer
RDRP reversible deactivation radical polymerization
ROMP ring-opening metathesis polymerization
ROP ring-opening polymerization
SB 4-(3-butenyl)styrene
siRNA short interfering ribonucleic acid
ssDNA single stranded DNA
SSO3Na sodium styrene-4-sulfonate
St styrene
StMe 4-methylstyrene
TBAm *N*-*tert*-butylacrylamide
tBA *tert*-butyl acrylate
TBDMS-OS 4-(tert-butyldimethylsilyloxy)styrene
tBS 4-(*tert*-butoxy)styrene
TEGDA triethylene glycol diacrylate
TEGMA (triethylene glycol monomethyl ether) methacrylate
TEGDMA triethylene glycol dimethacrylate
TESPMA 3-(triethoxysilyl)propyl methacrylate
TFEMA 2,2,2-trifluoroethyl methacrylate
TFPMA 2,2,3,3-tetrafluoropropyl methacrylate
TFPA 2,2,3,3-tetrafluoropropyl acrylate
THPA tetrahydropyran acrylate
TMSEA 2-(trimethylsilyloxy)ethyl acrylate
TMSEMA 2-(trimethylsilyloxy)ethyl methacrylate
TMAEMA 2-(trimethylamonium)ethyl methacrylate
TMAPMA 3-(trimethylamonium)propyl methacrylate
TPMMA triphenylmethyl methacrylate
VAc vinyl acetate
VB vinyl butyrate
VBA 4-vinylbenzaldehyde
VBSC 4-vinylbenzenesulfonyl chloride
VBDA (4-vinylbenzyl)dimethylamine
VBTAC (vinylbenzyl)trimethylammonium chloride
VBTPC (4-vinylbenzyl)trimethylphosphonium chloride
VBz vinyl benzoate
VF2 vinylidene fluoride
Vim 4-vinylimidazole
VPv vinyl pivalate
2VP 2-vinylypyridine
4VP 4-vinylpyridine

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