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RAFT polymerization to form stimuli-responsive polymers†

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Stimuli-responsive polymers adapt to their surrounding environment. These polymers are capable of responding to a variety of external stimuli, which include optical, electrical, thermal, mechanical, redox, pH, chemical, environmental and biological signals. They are encountered in many environments. They can have a variety of architectures (*e.g.*, copolymers, blocks, stars). They may be present as isolated macromolecules in a medium, as supramolecular assemblies, as smart coatings, as networks or some combination of these possibilities. This paper is concerned with the process of forming such polymers by radical polymerization with reversible addition fragmentation chain transfer (RAFT). RAFT polymerization has an advantage over most processes for reversible deactivation radical polymerization (RDRP) in its tolerance of a wide range of unprotected functionalities. Three basic strategies for forming stimuli-responsive polymers are considered: RAFT polymerization of functional monomers (a "grafting through" approach), the post-polymerization modification of RAFT-synthesized polymers (some combination of "grafting through", "from" and "to"), and the use of functional RAFT agents and RAFT end-group transformation (often "grafting from"). Other syntheses involve combinations of these processes and of RAFT polymerization with other processes. We also consider the responsiveness of the thiocarbonylthio-functionality of macroRAFT agents in terms of their ability to directly initiate and control RAFT polymerization and to regulate the properties of RAFT-synthesized polymers.

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Introduction

Stimuli-responsive polymers are capable of adapting to their environment. They respond to a variety of external stimuli that include optical, electrical, thermal, mechanical, redox, pH, chemical, environmental and biological signals.[1] This paper will not discuss the details of the many-fold applications and properties of stimuli-responsive materials, rather it is concerned at a more fundamental level with the processes of forming such functional polymers by RAFT (Reversible Addition Fragmentation chain Transfer) polymerization. We also largely exclude explicit coverage of biopolymer conjugates from this review. While these materials represent an extremely important class of stimuli-responsive polymers, their properties are adequately covered in other documents.[2,3] Moreover, in this review emphasis is placed on polymers which respond reversibly to a stimulus rather than polymers that undergo an irreversible change.

Stimuli-responsive elements of RAFT-synthesized polymers may originate from functionality present in the RAFT agent or macroRAFT agent, the monomers polymerized, or might be incorporated post-polymerization by transformation of the RAFT-synthesized polymer. Each of these possibilities will be considered. With the above constraints in mind, we commence with a brief overview of RAFT polymerization.

RAFT polymerization

RAFT polymerization[4] is a reversible deactivation radical polymerization (RDRP);[5] a process that, with appropriate attention to reagents and reaction conditions, can possess most of the attributes normally associated with living polymerization.[6,7] These attributes include, low molar mass dispersity, high end group fidelity, capacity for continued chain growth and access to complex architectures. RDRP are often called living or controlled radical polymerizations. However, the use of these terms in this context is now discouraged by IUPAC.[5]

The attributes of low molar mass dispersity, uniform chemical composition and high end group fidelity offered by RAFT polymerization are crucial to many applications in ensuring a reproducible, reliable and uniform response.

In the context of synthesis of stimuli-responsive polymers, RAFT polymerization has an advantage over other RDRP processes,[5] which include nitroxide mediated polymerization

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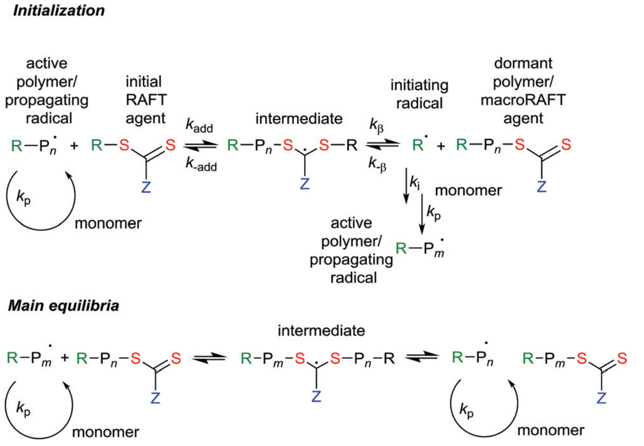


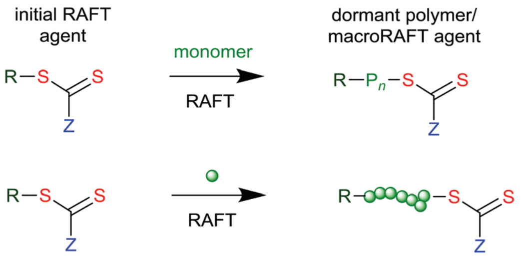
Scheme 1 Mechanism for reversible addition-fragmentation chain transfer. Initiation requires a source of radicals (initiation and termination reactions are not shown).

(NMP),[8,9] and atom transfer radical polymerization (ATRP) or transition metal-mediated RDRP,[10–15] in its tolerance of a wide range of functionalities in monomer, RAFT agent and the polymerization medium.

RAFT provides reversible deactivation by a degenerate chain transfer mechanism (Scheme 1). The chain transfer steps that comprise the main equilibria are termed degenerate because they involve only an exchange of functionality between propagating radicals and dormant polymer chains (called macroRAFT agents). The only distinction between the species on the two sides of the equilibria is their degree of polymerization (*n* and *m*). Moreover, in an effective RAFT process, where the rate of chain equilibration is rapid with respect to propagation, there should be less than one monomer unit added per activation cycle, so these also will be similar.

The overall RAFT process (Scheme 2) then comprises the sequential insertion of monomer units into an initial RAFT agent. The R and ZCS_2 groups are retained in the macro RAFT agent. The species labelled 'intermediate' in Scheme 1 should ideally be transient species and play no direct role in the process.

In that the steps comprise chain transfer reactions, there should be no net formation or loss of radicals as a consequence of the RAFT process. Initiating radicals must be formed in a separate step from an added initiator, from monomer, or from the RAFT agent. However, all radical species (initiating radicals, propagating radicals, even the intermediates) can, in principle, be involved in termination by radical–radical reaction. It is important to choose reaction conditions such that termination events are minimized. This generally means that targeted molecular weights should be substantially smaller than those that would be formed in a similar radical polymerization without the RAFT agent.



Scheme 2 Two representations of the overall RAFT Process.

Monomers in RAFT polymerization

While the reactivity of monomers in radical polymerization forms a continuum, it is useful to consider them as belonging to one of two broad classes.[16,17] The 'less activated' monomers or LAMs (see Fig. 1) are those where the double bond is adjacent to one or more oxygen, nitrogen, halogen or sulfur lone pairs [*e.g.*, vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP), *N*-vinylcaprolactam (VCL), 5,6-benzo-2-methylene-1,3-dioxepane (BMDO), vinyl chloride (VC), vinylidene fluoride (VF2), (4-bromophenyl)(vinyl)sulfane (BPVS)] or saturated carbon (*e.g.*, diallyldimethylammonium chloride (DADMAC), BOC-protected allylamine (ABOC)).

The 'more-activated' monomers (MAMs, see Fig. 2) are those where the double bond is conjugated to an aromatic ring [*e.g.*, the styrenes and vinyl aromatics: styrene (St) and substituted styrenes, 4-vinylpyridine (4VP), acenaphthalene (AcN)], a double bond [*e.g.*, the dienes: butadiene (Bd), isoprene (Ip), chloroprene (Cp)], a carbonyl group [*e.g.*, methacrylic acid (MAA), methyl methacrylate (MMA), acrylic acid (AA), methyl acrylate (MA), acrylamide (Am)] or a nitrile [*e.g.*, acrylonitrile (AN)]. Maleic anhydride (MAH) and maleimides [*e.g.*, *N*-phenylmaleimide (NPMI)] also belong to this class.

As with any continuum some monomers fall at the boundary of the extremes. Thus, *N*-vinylcarbazole (NVC), and most

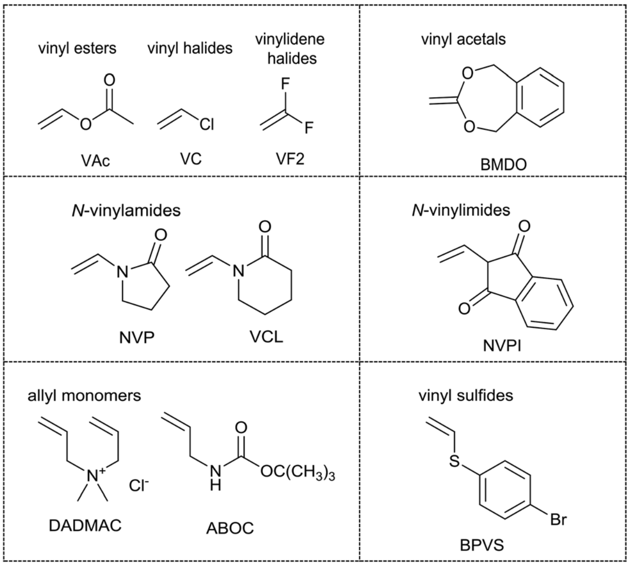


Fig. 1 Abbreviations for and examples of some less-activated monomers (LAMs). Polymer abbreviations are formed by including the monomer abbreviation in parentheses and suffixing with "P", *e.g.*, P(VAc) is poly(vinyl acetate).

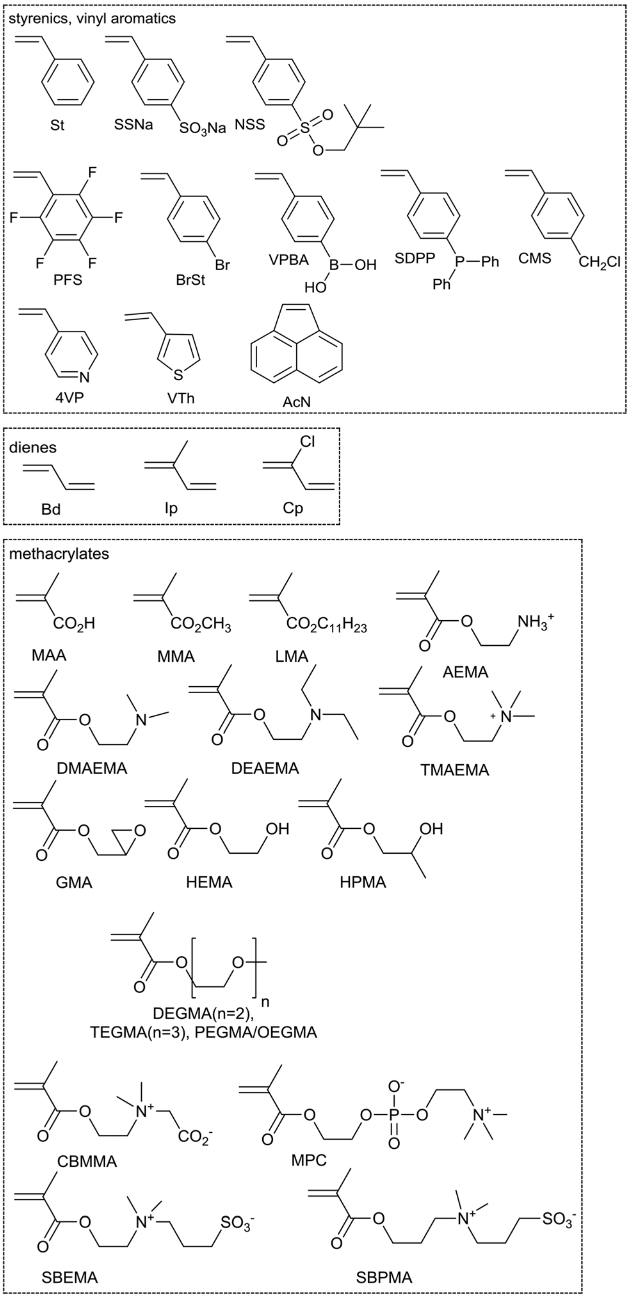


Fig. 2 Examples of some more-activated monomers (MAMs). Polymer abbreviations are formed by including the monomer abbreviation in parentheses and suffixing with "P", *e.g.*, P(St) is polystyrene.

likely other *N*-vinyl aromatics, are intermediate stabilized monomers (IAMs).[18]

To date, most syntheses of stimuli-responsive polymers have involved the polymerization of MAMs. The reason for this is partly historical, reflecting the fact that most RDRP processes (*e.g.*, ATRP and NMP) are not generally applicable to LAMs (or IAMs).

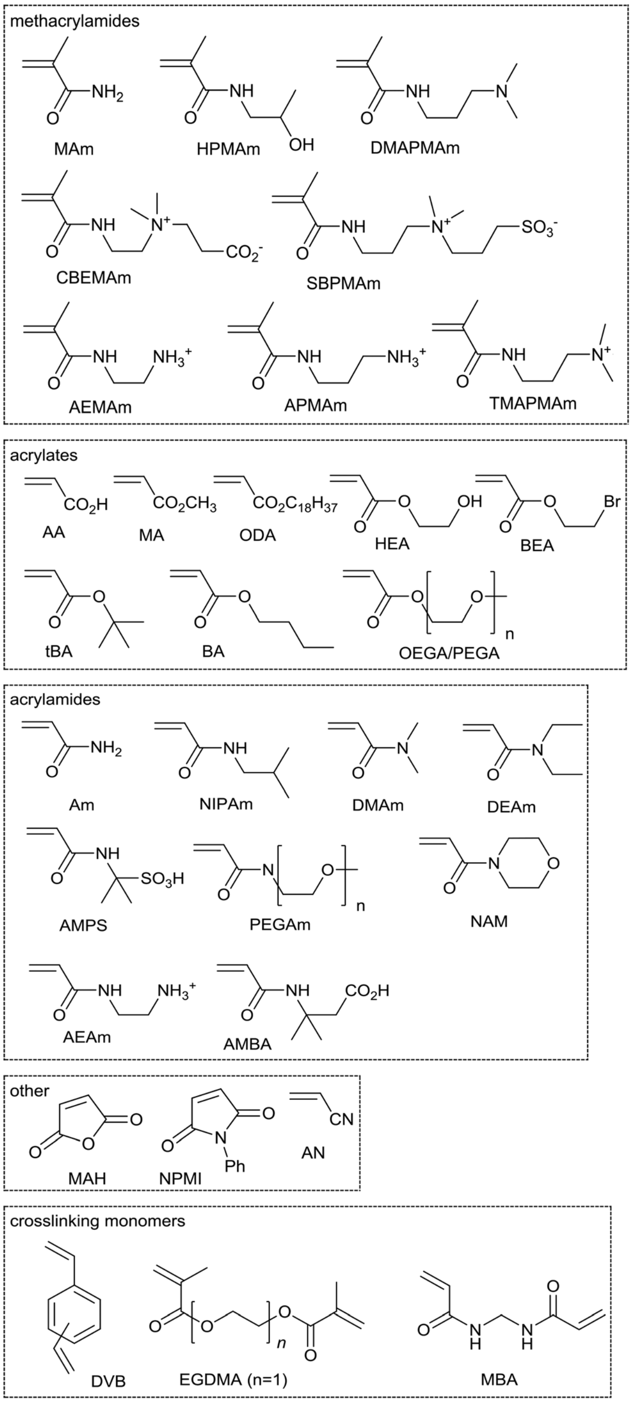


Fig. 2 *(Contd).*

With appropriate selection of the RAFT agent, RAFT polymerization is compatible with all monomer classes. Indeed, the polymerization of most monomers amenable to radical polymerization can be mediated by RAFT. The exceptions are those that contain functionality that may react with the thiocarbonylthio group of the RAFT agent. Of specific concern are monomers which contain nucleophilic substituents such as primary or secondary amino-, or thiol-substituents. For example, RAFT polymerization of AEMA as the free amine is not well-controlled. However, low dispersity P(AEMA) can be successfully prepared when the monomer is maintained in fully protonated form. RAFT polymerization can be performed for monomers containing primary aromatic amines (*e.g.*, **53**,[19] see section *Nitric oxide responsive polymers*).

Monomers that are not readily polymerized by conventional radical polymerization, *e.g.*, those that contain functionality that is reactive toward the propagating radicals (such as nitro-groups[20]), are also likely to be problematical in RAFT polymerization (or other RDRP). Nonetheless, RAFT does offer, some benefits in this context. For example, it is possible to achieve higher monomer conversions without gelation (significant crosslinking) in RAFT (co)polymerization of the conjugated diene monomers, butadiene (Bd), isoprene (Ip) and chloroprene (Cp), than in conventional radical polymerization.[21] This result can be attributed to the lower dispersity of the RAFT-synthesized (co)polymers and, in particular, to the elimination of the high molecular weight tail of the molecular weight distribution.

Factors limiting the control exerted in RDRP of LAMs are the relatively high incidence of propagation involving head addition to monomer and of irreversible chain transfer. This has been studied for RAFT polymerization of VAc[22,23] and VF2[24] and may be significant for other LAMs which show some proclivity for head addition during radical polymerization.[25] Interestingly, RAFT polymerization of VC[26] and of certain vinyl ethers[27] has been found less problematical than would have been expected on the basis of studies of the conventional process.

Theoretical arguments suggest that side reactions that involve rearrangement of transient intermediates (propagating species) should be less prevalent in RDRP, which impacts, in particular, on RDRP of acrylates, VAc and VC.[28]

RAFT agents

RAFT agents, their design, selection and synthesis, are well-described in recent reviews.[16,17,29–32] The choice of the initial RAFT agents (ZC(=S)SR) for a set of monomer(s) and reaction conditions is crucial to achieving good control over dispersity and end-group fidelity. The effectiveness of RAFT agents is determined by the substituents Z (the activating group) and R (the homolytic leaving group). General guidelines for their selection are summarized in Fig. 3 and 4, respectively.[16,32]

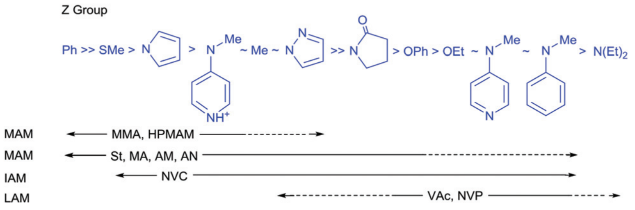


Fig. 3 Guidelines for selection of the 'Z' group of RAFT agents (Z–C(=S)S–R) for various polymerizations. RAFT agent addition rates and transfer constants decrease and fragmentation rates increase from left to right. For 'R', fragmentation rates decrease from left to right. A dashed line indicates limited control (*e.g.*, retardation and/or high dispersity likely under some conditions). Figure updated from the similar guidelines that appeared in earlier reviews.[32,47] For monomer abbreviations see Fig. 1 and 2.

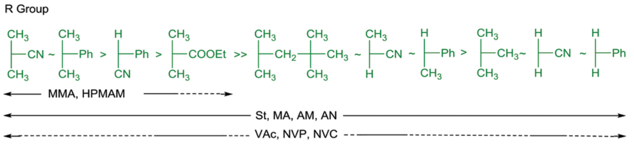
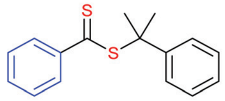
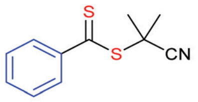
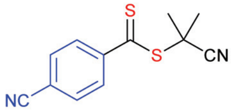
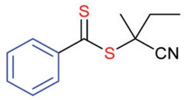
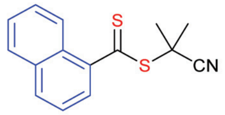
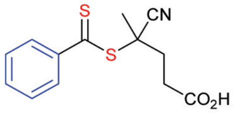
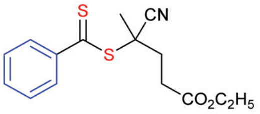
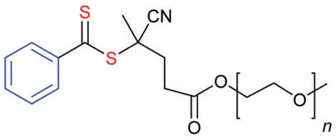
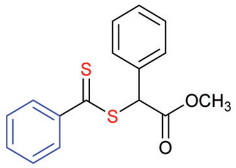
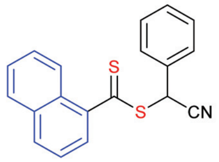
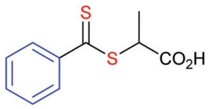
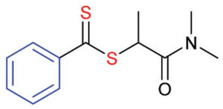
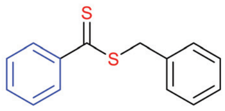
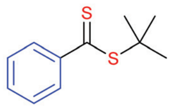


Fig. 4 Guidelines for selection of the 'R' group of RAFT agents (Z–C(=S)S–R) for various polymerizations. Fragmentation rates decrease from left to right. A dashed line indicates limited control (*e.g.*, retardation and/or high dispersity likely under some conditions). Figure updated from the similar guidelines that appeared in earlier reviews.[32,47] For monomer abbreviations see Fig. 1 and 2.

Table 1 Aromatic dithioester RAFT agents

 **1**	 **2**
 **3**	 **4**
 **5**	 **6**
 **7**	 **8**
 **9**	 **10**
 **11**	 **12**
 **13**	 **14**

RAFT agents referred to in the text are shown in Table 1 (aromatic dithioesters), Table 2 (trithiocarbonates), Table 3 (dithiocarbonates or xanthates) and Table 4 (dithiocarbamates).

Z group selection. It was pointed out some time ago[32] that, with access to just two types of RAFT agent differing in the Z group, it is possible to control the polymerization of most

Table 2 Trithiocarbonate RAFT agents

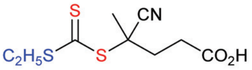
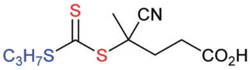
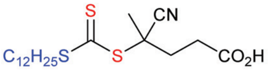
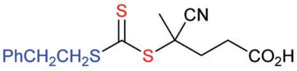
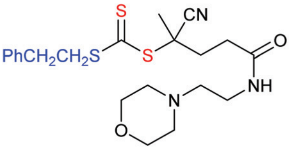
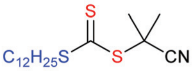
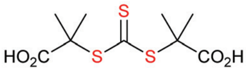
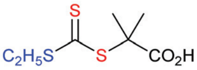
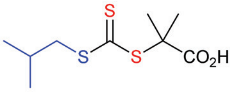
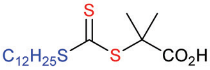
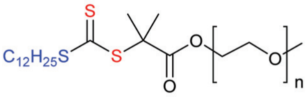
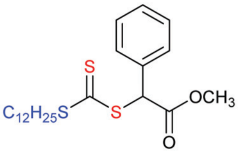
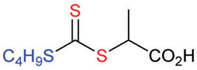
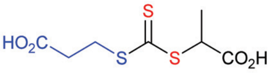
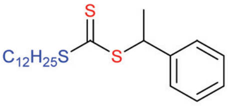
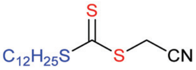
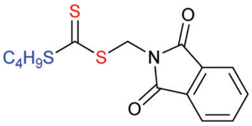
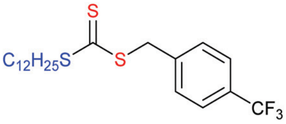
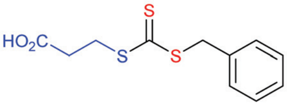
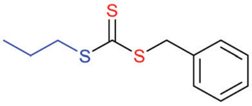
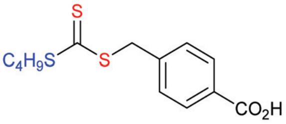
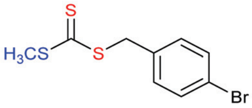
 **15**	 **16**
 **17**	 **18**
 **19**	 **20**
 **21**	 **22**
 **23**	 **24**
 **25**	 **26**
 **27**	 **28**
 **29**	 **30**
 **31**	 **32**
 **33**	 **34**
 **35**	 **36**

Table 3 Xanthate or dithiocarbonate RAFT agents

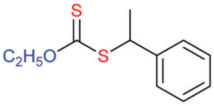
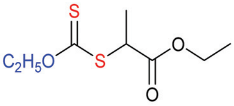
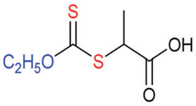
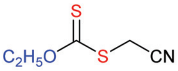
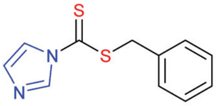
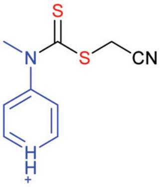
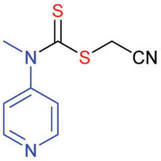
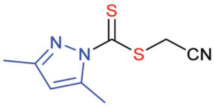
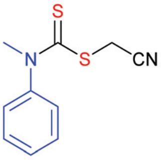
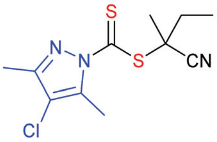
 **37**	 **38**
 **39**	 **40**

Table 4 Dithiocarbamate RAFT agents

 **41**	 **42**
 **43-H$^+$**	 **43**
 **44**	 **45**
 **46**	

monomers so as to provide low dispersities, high end group fidelity and minimal retardation.[32] One RAFT agent would be suited to MAMs (*e.g.*, a trithiocarbonate) and the other to LAMs (*e.g.*, a xanthate or dithiocarbamate).

Aromatic dithioesters such as the dithiobenzoates are amongst the most active RAFT agents (Fig. 3) and are arguably the reagents of choice for methacrylates and methacrylamides.[33] They are, however, also more prone to side reactions, which include hydrolysis. Polymerizations of monosubstituted MAMs may be retarded by dithiobenzoates and those of LAMs and IAM are often inhibited. This is attributed to the "intermediate" species (Scheme 1) having a sufficient lifetime that some are consumed in side reactions. The polymerizations may also show greater oxygen sensitivity.

Trithiocarbonates, while not as active as the dithiobenzoates, provide a better balance between activity and incidence of side reactions. They are currently the most popular RAFT agents for controlling polymerization of MAMs.[34,35]

The dithiocarbonate (or xanthate)[36] and dithiocarbamate[37–40] RAFT agents towards the centre of Fig. 3 provide a measure of control over the polymerization of both MAMs and LAMs.

Recent examples of such RAFT agents are the 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates.[41] These dithiocarbamates have wide-spread applicability. The cyanomethyl-derivative **44** offers very low dispersities ($Đ < 1.1$) for MAM-derived polymers P(MA), P(DMAm) and P(St) and $Đ < 1.3$ for the LAM, P(VAc).[41] The 4-chloro-3,5-dimethyl-1*H*-pyrazole-1-carbodithioate **46** provides reasonable control ($Đ \sim 1.3$) in MMA polymerization.[42]

Switchable RAFT agents (*e.g.*, **43**/**43-H**$^+$), so-called because they can be reversibly switched by an external stimulus to give very good control over polymerization of either MAMs or LAMs, have been also described[43,44] Protonation provides a pH switch in most current examples. As indicated in Fig. 3, the unswitched **43** is similar to **45** in activity and provides good control over LAMs (*e.g.*, VAc), while the switched **43-H**$^+$ has similar activity to **42** and is effective with MAMs (*e.g.*, St). These RAFT agents are further discussed below (see *Switchable (pH responsive) RAFT agents*).

In the context of stimuli-responsive polymer synthesis, requirements for specific end-group-functionality, architecture and/or solubility characteristics will also play a role in dictating the selection of the type of RAFT agent.[45,46]

R group selection. The R group of the initial RAFT agent (ZC(=S)SR) must be selected to equal or better the homolytic leaving group ability of the propagating radical(s) formed in polymerization and also be a good initiating radical for the monomer(s) being polymerized. The rate constant for reaction of the radical R$^\bullet$ with monomer (k_i) should be greater than or equal to that for propagation (k_p).

When k_i is substantially lower than k_p, polymerizations may be subject to an inhibition period until the initial RAFT agent is converted to a macroRAFT agent. This situation pertains in the case of more highly stabilized or sterically hindered radicals that are good homolytic leaving groups but add to monomer only slowly, *e.g.*, when the RAFT agent R group is benzyl or substituted benzyl and the monomer is a LAM or IAM. This behaviour accounts for some of the dashed lines in Fig. 4. It does not mean that low dispersity polymers cannot be formed at higher monomer conversions. However, the behaviour can result in an inhibition period and places a constraint on the end-group fidelity.

RAFT agents for stimuli-responsive polymers. RAFT agents that have found use in the context of synthesis of stimuli-responsive polymers are shown in Tables 1–4. In selecting RAFT agents for use in polymerization there are many factors to consider other that the reactivity or the RAFT agent.

For homogeneous RAFT polymerization, the solubility of the RAFT agent in the polymerization medium, can be a key concern. Aqueous soluble RAFT agents are of particular interest for many bio-applications and also for the synthesis of thermoresponsive polymers.[48–50] RAFT agents which show a degree of water solubility include **6**, **8**, **12**, **15**, **21**, **22**, **28**, **39** and **43**/**43H**$^+$.[51] Note that some require at least partial ionization for solubility.

For heterogeneous polymerization, the solubility of the RAFT agent determines whether the RAFT agent or macroRAFT is localized in the desired phase and the transport/partitioning of the RAFT agent between phases.[52,53] The selection of RAFT agents for emulsion and other forms of heterogeneous polymerization is complex and space limitations prevent a detailed discussion.

The selection of RAFT agent must also take into account the functionality required for the end-use application and whether thiocarbonylthio group removal/transformation is required. It is important to note that the Z group and its functionality will typically be lost if the RAFT end group is cleaved (see *RAFT end-group transformation chemistry*).

Initiators in RAFT polymerization

The RAFT mechanism (Scheme 1) requires an external source of radicals for polymerization to proceed. The initiators used in RAFT polymerization are most commonly a thermal source of radicals such as 2,2′-azobis(2-methylpropanenitrile), AIBN.[54] However, other initiators, including various peroxides, can also be used. Even though the peroxide-derived radicals may react irreversibly with RAFT agents, the kinetic parameters[55] generally ensure that oxygen-centred peroxide-derived radicals react preferentially with monomer under most polymerization conditions.

The initiating radicals may also be formed from directly from the monomer (*e.g.*, in thermal St polymerization[56]), or from the RAFT agent by direct photolysis,[57–62] or by redox (*e.g.*, by atom transfer radical addition)[63,64] or photo-redox chemistry.[65–70] The redox- and photo-responsiveness of the RAFT agent thiocarbonylthio-functionality, and photo electron/energy transfer-RAFT (PET-RAFT), are considered further later in this review.

In RAFT polymerization, the rate of initiation should be as low as possible commensurate with achieving an acceptable rate of polymerization. When conventional initiators are used the usual guideline is that the amount of initiator (or more correctly, the amount of initiator-derived radicals formed) should be less than 10 mole% of the amount of RAFT agent. This should ensure an end-group fidelity of greater than 90%.

The fraction of living chains (L) in RDRP is defined as the number of active chain ends plus the number of dormant chain ends. In a RAFT polymerization, this equates to the fraction of chains with RAFT agent functionality and can be estimated from the relationship (eqn (1)):[32]

$$L = \frac{[\mathrm{T}]_0}{[\mathrm{T}]_0 + df([\mathrm{I}]_0 - [\mathrm{I}]_t)} \tag{1}$$

where $[\mathrm{T}]_0$ is the RAFT agent concentration, d is the number of chains produced from radical–radical termination (1.0 for termination by combination, 2.0 for termination by disproportionation), f is the initiator efficiency and $[\mathrm{I}]_0 - [\mathrm{I}]_t$ is the initiator consumed. The expression applies to initiators which decompose to form two similar radicals, such as AIBN. If the initiator decomposition rate constant (k_d) is known,[54] the initiator consumption at time t can be estimated using eqn (2):

$$[\mathrm{I}]_0 - [\mathrm{I}]_t = [\mathrm{I}]_0 \ (1 - e^{-k_d t}) \tag{2}$$

In cases where polymerization is slow, rather than boost the rate of initiation, a better strategy when possible is to choose conditions that facilitate propagation (*e.g.*, by increasing the temperature and/or the monomer concentration).

In order to maximize RAFT end-group fidelity and/or block purity, it is important to stop the polymerization once the desired conversion is achieved. Continued production of radicals beyond this point will lead to further loss of living ends.

One criticism of RAFT, in comparison to RDRP such as NMP or ATRP, is that because an exogenous initiator is used in RAFT there must be (a greater number of) dead chains. However it should also be noted that both the rate of polymerization and the rate of termination are determined by the radical concentration. It follows that all RDRP that proceed at a similar rate will experience a similar amount of termination.

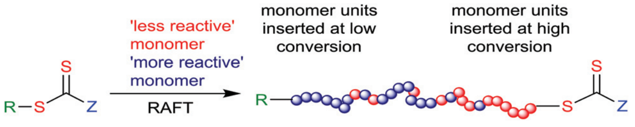
Gradient copolymer synthesis

In a random copolymer, the polymer composition and sequence distribution are determined only by the concentrations of monomers in the feed. In a statistical copolymer, the polymer composition and sequence distribution is additionally determined by the monomer reactivity ratios. Random copolymers, alternating copolymers and gradient copolymers are each a subset of statistical copolymers that may be formed depending on the polymerization method and the monomer reactivity ratios.[71]

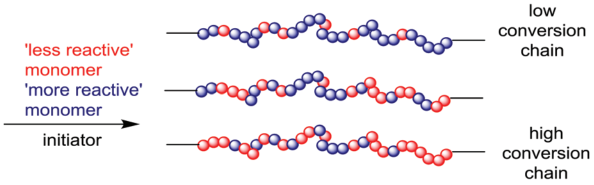
Most copolymers formed by RAFT copolymerization of two or more monomers will, by default, be gradient copolymers. Any compositional drift that arises from disparities in the reactivity ratios will be captured within each individual polymer chain. The more reactive monomer will appear closer to the "R" end. The less reactive monomer(s) will be concentrated at the "ZCS_2" end (Scheme 3). In RAFT copolymerization, chains will not be identical but all will possess the same gradient composition with the monomer sequence distribution being determined by the monomer reactivity ratios.

Forced gradient copolymers are made by purposefully skewing the monomer feed.[72,73] Any changes in monomer composition will be immediately reflected in the composition of each polymer chain at the "ZCS_2" end. Feed addition protocols can be designed to form random copolymers when reactivity ratios would dictate that a gradient would be formed for a batch polymerization. In batch heterogeneous polymerization, gradient compositions may also reflect the differential solubility of the monomers.[74]

In the context of forming stimuli-responsive copolymers, an important benefit of RAFT polymerization and gradient copolymer formation, is that all chains formed have essentially the same composition. In these circumstances, conventional radical copolymerization of monomers with disparate reactivity ratios would yield a polymer blend (Scheme 4). In the conventional (non-RDRP) process, polymer chains formed at low monomer conversion will differ in composition and molar mass from those formed at high conversion. This behaviour provides one explanation for RAFT-synthesized copolymers showing properties that are substantially different to those of conventionally prepared copolymers in various applications. Examples of stimuli-responsive polymers which take advantage of such spontaneous gradient formation include RAFT copolymerization of St with AA.[75] Particularly disparate reactivity ratios enables the RAFT-synthesis of "blocky" copolymers in a batch process (*e.g.*, in copolymerizations of St with MAH[76,77] or in the copolymerization of ODA with NVP[78,79]) and allows the concept of "writing to polymer chains" by shot addition of small amounts of monomer during polymerization.[80,81]



Scheme 3 RAFT gradient copolymer synthesis making use of two monomers with disparate reactivity ratios.



Scheme 4 Conventional copolymer synthesis making use of two monomers with disparate reactivity ratios will form a blend. Chains formed at low conversion will comprise mainly the more reactive monomer.

A recent example of gradient polymer synthesis in the context of stimuli-responsive polymers is the synthesis of gradient polymer electrolytes for application in lithium batteries.[82]

Good control in RAFT MAM/LAM copolymerization is possible in circumstances where a given RAFT agent may be specific for MAMs or LAMs. Thus, trithiocarbonates provide good control in copolymerizations of *t*BA and VAc even though the same RAFT agent inhibits VAc homopolymerization. Xanthates and dithiocarbamates also provide good control in such copolymerizations (*e.g.*, **40** in MA/VAc copolymerization[83] or **20** in DMAm/VAc copolymerization[41]).

Non-gradient (random) copolymer synthesis

In forming stimuli-responsive polymers it is sometimes desirable to have monomer functionalities randomly distributed within copolymer chains. As stated above, the default product in RAFT copolymerization (and other RDRP) will be a gradient copolymer. Random copolymers will only be formed when the monomer reactivity ratios are unity (*e.g.*, copolymerization of two similar methacrylates approach this ideal), when a constant ratio of monomers in the feed can be maintained by judicious additions of monomer(s), and when copolymerizations are performed at an azeotropic monomer composition.

For binary copolymerizations of two monomers A and B that can be represented by the terminal model,[84] and where the monomer reactivity ratios are both greater than or less than unity, there will be exactly one azeotropic composition for the monomer feed when the fraction of monomer A in the feed (f_A) is $(1 - r_A)/(1 - r_B)$.[84] In RAFT copolymerization this value may be perturbed for short chain lengths by specificity shown by the RAFT agent-derived radical. Conditions for azeotropic compositions for binary copolymerization when a penultimate model applies[85] and for ternary and quaternary copolymerizations[86] have also been defined.

In the context of RAFT copolymerization, polymerization under azeotropic conditions has been made use of in forming, *e.g.*, St/MMA[87] St/Bd[88] and St/AN copolymers.[4] Moraes *et al.* have explored the strategy for the case of HPMA copolymers.[89]

Sequence defined polymers by RAFT

There is much interest been in the preparation of sequence defined polymers by RAFT and other RDRP wherein the sequence of monomers in a polymer chain is decided by the synthetic chemist rather than statistical factors. The goal is to attain the precision demonstrated by nature in molecules such as proteins or nucleic acids. The development of a practical strategy should immediately lead to a major advance in stimuli-responsive polymers.

Multi-block polymer synthesis. Many have decided that that sequence control and the monomer level is impractical and have turned their attention to the production of multi-block copolymers in which the sequence of blocks is controlled. This approach is described in the section Block copolymer synthesis below.

RAFT single unit monomer insertion. RAFT single unit monomer insertion (SUMI) was demonstrated by Zard and coworkers[90] as a useful technique in organic synthesis, a decade before the invention of the RAFT as a method for RDRP. Much recent interest placed in performing sequential SUMI to form copolymers with sequence distribution that is precisely defined at the monomer level. Using conventionally initiated RAFT with appropriate selection of RAFT agent and monomer, high yield (>95%) SUMI has been demonstrated for monosubstituted MAMs (*e.g.*, St,[91,92] 2-vinylthiophene,[93] DMA,[92] NIPAM[91]). Successful SUMI requires a RAFT agent with C_{tr} such that, on average, there is <1 monomer inserted per activation cycle (*i.e.*, $k_p[M] \ll k_{tr}$[RAFT agent]) and is facilitated by $k_i \gg k_p$, by $k_\beta \gg k_{-add}$ (refer Scheme 1), by low relative monomer concentrations (stoichiometric with RAFT agent) and an initiator-derived radical that is identical to the RAFT agent 'R' group.[91,92] SUMI is an important technique for converting macromonomers to macroRAFT agents.[93]

In cases where high yield SUMI is not possible, the application of separation techniques, such as preparative recycling size exclusion chromatography,[94–96] can enable separation of discrete oligomers from the reaction-derived oligomer mixtures. However, yields are then lowered.

Consecutive high yield SUMI has been demonstrated for St-MAH[92] and St-NPMI co-dimer[97] with **2**. Success in these cases can be attributed to MAH and NPMI being inert to the initiator-derived radical from AIBN. Zard and co-workers[98] reported consecutive SUMI of NVPI followed by an allyl monomer into a xanthate. A key factor contributing to success in these examples is the use of a non-homopolymerizable monomer[99] ($k_p \sim 0$) in the second SUMI step. However, in general, yields in conventionally initiated consecutive SUMI experiments are substantially lowered by the concurrent formation of products from initiator-derived chains.[91,92] SUMI of non-homopolymerizable monomers also provides a method of chain-end functionalization for RAFT synthesized polymers. MAH,[100–103] maleimides,[104,105] β-pinene,[105] and ABOC (for a primary amino end-group)[106] have been used in this context.

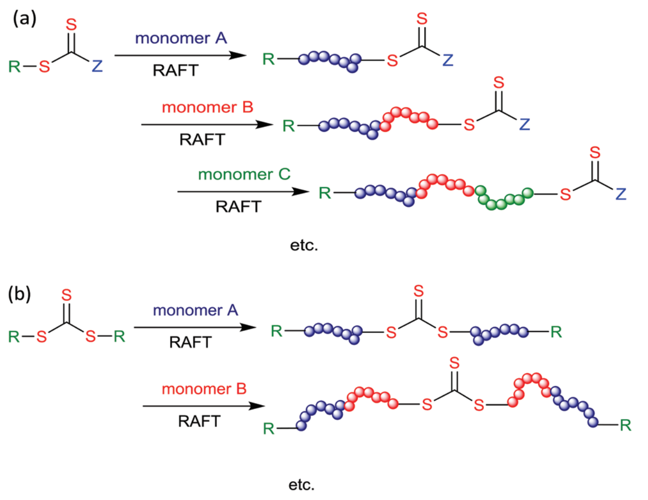
A recent development is PET-RAFT-SUMI wherein radicals are generated directly by photo-activation of the RAFT agent (see section on *Light-responsive RAFT agents* below). It has been possible to form discrete, *e.g.*, St-NPMI-VAc co-trimers in near quantitative yield.[107] The full scope of this process is currently being explored.

Template polymerization. The use of templates, many biologically derived or at least biologically inspired, has been studied.[108] One approach makes use of polymers comprising nucleobase pendants with the aim of preparing precisely defined daughter polymers of the complementary nucleobase.[109–111]

Block copolymer synthesis

Di-, tri- and higher order block copolymers or multi-blocks can be simply made by sequential addition of monomers (Scheme 5).[112] Details are provided in many reviews.[17,32,113] However, it is worthwhile stressing some of the critical factors for achieving high quality blocks.

The factors mentioned above under Initiators in RAFT polymerization with respect to maintaining end-group fidelity are also extremely important to attaining block purity in block copolymer synthesis.[112] For each chain initiated, between one and two chains will terminate depending on the termination mechanism. Thus, in making an AB diblock, there will be an amount of homopolymer A contaminant corresponding to the



Scheme 5 Representations of RAFT multi-block copolymer synthesis by sequential monomer addition using (a) a mono-RAFT agent or (b) a symmetrical trithiocarbonate.

number of initiator-derived chains generated during the synthesis of the A block. Any Initiator-derived chains formed during formation of the B block will comprise a homopolymer B impurity. Moreover, if termination occurs by combination, some ABA triblock will also be formed during this step. The situation become progressively more complex for multi-block copolymers, as the number of generations increases.

For high k_p monomers such as acrylates and acrylamides, it is possible to achieve high polymerization rates with very low amounts of initiator. It is, therefore, also possible to achieve high (*e.g.*, >99%) monomer conversions whilst maintaining the integrity of the RAFT end groups. For example, this strategy was to advantage used in making amphiphilic copolymers comprising a P(ODA) block,[79] where any residual ODA is difficult to remove. It was also applied in the Perrier approach[114–117] to multi-block copolymer synthesis.

Nonetheless, in order to maximize end-group fidelity, it is desirable to limit monomer conversion to *e.g.*, <90%, particularly in the case of low k_p monomers such as styrenes and methacrylates. As monomer conversion increases, termination becomes progressively more important. In these cases, it may be expedient to prepare what have been called quasi-block copolymers.[118,119] These arise when block copolymers are formed by sequential addition of monomers where there is incomplete monomer conversion and no purification is performed to remove the residual monomer. For the case of sequential addition of two monomers A and B, the product "quasi-block" will be a gradient copolymer, P(A)-*b*-P(A-*grad*-B), due to the incorporation of the residual first block monomer into the second block. The detailed structure of the "quasi-block" will depend on the monomer reactivity ratios. Where reactivity ratios are similar (*e.g.*, for copolymerization of several methacrylates[120]) the copolymer structure may approximated as P(A)-*block*-P(A-*ran*-B). Where the monomer reactivity ratios are such that there is a strong tendency for alternation (*e.g.*, St/MAH), the copolymer structure will be P(A)-*b*-P(A-*grad*-B)-*b*-P(B). The quasi-block protocol is particularly attractive when using high-throughput methods.[119–121] However, the impact on polymer properties always needs to be considered. For many applications, purity is of paramount importance.

The factors that were mentioned as important for *R group selection* above also determine the order in which blocks should be constructed in block copolymer syntheses based sequential monomer addition. The propagating radical derived from the first-made block must be a good homolytic leaving group (*i.e.*, equal or better) with respect to that to be produced from the monomers of the next-made block. The propagating radical derived from the first-made block must add efficiently to at least one of the monomer(s) that will comprise the second block.

For example, in attempted synthesis of P(St-*b*-VAc) the P(St) propagating species adds VAc only slowly.[43] As a consequence, the P(St) macroRAFT agent is only slowly consumed, there is significant retardation particularly in the presence of any residual St monomer, and, even though a low dispersity diblock is possible, complete conversion to a diblock is only achieved for high monomer conversions. This situation can be remedied by installing a short block of a more suitable monomer (MA) between the P(St) and P(VAc) blocks to form P(St)-*b*-P(MA)-*b*-P(VAc).[43,122] The P(MA) block length should be sufficient to ensure at least one unit of MA at the end of every chain. A second remedy is to add a small amount of MA as a comonomer in forming the VAc block [to form P(St)-*b*-(P(MA)-*grad*-P(VAc))-*b*-P(VAc)]. The St/MA and MA/VAc reactivity ratios are such as to ensure the desired structure.[43,122]

Another method of achieving improved block integrity when constructing "wrong-way" blocks, or when using low transfer constant macroRAFT agents, involves use of starved-feed addition protocol.[123,124] The rate of consumption of an initial RAFT or macroRAFT agent can be approximated by the expression (eqn (3))

$$\frac{d[\mathrm{RCS_2Z}]}{d[\mathrm{M}]} \approx C_{\mathrm{tr}} \frac{[\mathrm{RCS_2Z}]}{[\mathrm{M}] + C_{\mathrm{tr}}[\mathrm{RCS_2Z}] + C_{-\mathrm{tr}}[\mathrm{RP}_n\mathrm{CS_2Z}]} \qquad (3)$$

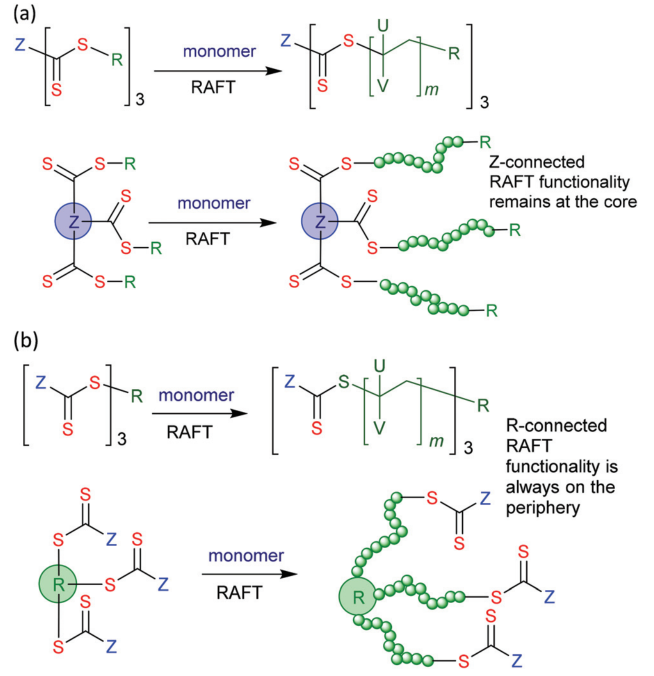
where C_{tr} (= $[k_{\mathrm{add}}/(k_{-\mathrm{add}} + k_{\beta})]/k_{\mathrm{p}}$) and $C_{-\mathrm{tr}}$ (= $[k_{-\beta}/(k_{-\mathrm{add}} + k_{\beta})]/k_{\mathrm{i}}$) are the forward and reverse transfer constants associated with the initialization process (refer Scheme 1). This indicates that the relative rate of consumption of the initial RAFT agent can be enhanced by reducing the monomer concentration. In early work, this strategy was employed in preparing low dispersity block copolymers from so-called macromonomer RAFT agents.[125,126] Very recently, this strategy has been applied in the synthesis of multi-block copolymers.[127]

Star polymer synthesis

Star structures and the general approaches to star polymer synthesis are described in detail in a recent review.[128] There are two main routes to star polymers by RDRP. These are (a) the core-first methods, in which chains are grown from a core containing multiple RAFT agent functionalities (a "grafting from" approach) and (b) the arm-first methods, in which arms are prepared first and linked to provide a star structure (may be "grafting to" or "grafting through").

Particularly For the case of core-first methods that involve RAFT polymerization, we should additionally consider processes based on Z-connected or R-connected RAFT agents (Scheme 6). These are sometimes known as the convergent- and divergent-growth approaches, respectively. For the process based on Z-connected RAFT agent propagating radicals are always detached from the core. Dormant chains are attached to the core by a cleavable thiocarbonylthio linkage. No star–star coupling is likely. For the process based on R-connected RAFT agents most propagating radicals remain attached to the core (initiator-derived chains whether active or dormant remain detached from the core). The polymer is directly attached to the core and the thiocarbonylthio group is an end group. Star–star coupling is frequently observed.

The core in core-first star synthesis can be a well-defined low molecular weight compound.[123,129] However, a wide range of multifunctional substrates can be converted to multi-RAFT



Scheme 6 Representation of core-first processes for 3-arm star synthesis by RAFT polymerization with (a) Z-connected and (b) R-connected RAFT agents.

agents using well-established chemistry.[130] These substrates may take the form of:

- a dendrimer, a hyperbranched oligomer/polymer, or a nano- or microgel.
- a particle or nanoparticle.[131,132] See *Surface-initiated RAFT polymerization (SI-RAFT)* below.
- a metal complex[133–140] There are now many examples of using metal complexes directly as the core of star polymers. The metal complex must be compatible with the redox properties of RAFT agent.

The early CSIRO work[129] showed that low dispersity stars could be synthesized making use of both Z-connected and R-connected multi-RAFT agent cores. Later work established mechanisms for accelerated termination in polymerizations with Z-connected RAFT agents.[141] This has served to emphasize the importance of RAFT agent design and the choice of polymerization conditions.[142]

Two convenient processes for forming nanogel cores by RAFT polymerization are RAFT-mediated crosslinking copolymerization[143,144] and RAFT self-condensing vinyl polymerization.[145–149] The crosslinking copolymerization approach involves RAFT mediated copolymerization of a multi-olefinic crosslinking monomer *e.g.*, DVB, EGDMA or MBA. The self-condensing vinyl polymerization route involves RAFT (co) polymerization mediated by a RAFT agent containing monomer functionality (sometimes these are referred to as RAFT inimers). Recently, we compared these two approaches in preparing star architectures for antigen delivery.[150]

The arm-first route often involves a crosslinking copolymerization mediated by a macroRAFT agent.[151,152] The method involving RAFT polymerization was first described in patent applications that appeared during 1999–2000 by Solomon *et al.*[153] and Berge *et al.*[154] A variant on the approach makes use of a macromonomer, a crosslinking agent and a low molecular weight RAFT agent.[155] Examples of arm-first star synthesis making use of redox sensitive crosslinkers comprising a disulphide linkage can be found in Table 7.

The optimal conditions for achieving low dispersities when preparing RAFT-synthesized stars by the arm-first process are not fully understood. Some early studies found that the use of RAFT polymerization in the arm-first method provided polymers with a relatively broad molar mass distribution.[156] The use of heterogeneous (emulsion) polymerization has been advocated to resolve this issue.[157,158] For homogeneous polymerization, the dispersities of star polymers appear strongly solvent dependent. It was suggested that one requirement for attaining low dispersities that polymerization medium is a poor solvent for the crosslinker.[159,160] Low dispersity stars (POEGA, P*t*BA or PNIPAm arms) were obtained with use of the crosslinker *N*,*N*′-bis(acryloyl)cystamine in toluene as solvent.[159] However, this appears to be neither a necessary nor a sufficient condition for forming low dispersity stars and further study is needed.[161]

In the arm-first process the RAFT functionality is retained in the core. Thus arm-first stars can be used subsequently as macroRAFT agents in the so called "in–out" process for mikto-arm star synthesis.[162] Mikto-arm stars comprise arms of two or more different compositions attached to a central core[163,164] and various approaches using RAFT polymerization have been applied in their synthesis.[100,152,165–172]

Cylindrical polymer brushes

In this section, we consider so-called bottle brush polymers or cylindrical polymer brushes. Brushes formed on surfaces or particles are discussed below under SI-RAFT.[173]

Strategies for bottle brush polymers and cylindrical polymer brush synthesis by RAFT polymerization generally parallel those already described for star polymer synthesis. Thus, core-first approaches have been described that commence with synthesis of polymers with pendant RAFT agent functionality.[174–176] In the case of low k_p monomers (*e.g.*, St, MMA) use of a "sacrificial" RAFT agent has been shown to facilitate synthesis R-connected polymer brushes.[177]

Arm-first approaches usually involve polymerization of macromonomers; a "grafting through" strategy. Examples are generally limited to those monomers that are sterically less demanding such as, PEGA,[178] PODA,[79,179,180] and the corresponding methacrylates.

Other methods involve formation of a functional polymer backbone and brush formation by some combination of RAFT polymerization, "click" chemistry, and sometimes another RDRP method, most commonly ATRP. Examples include:

- the syntheses of alkyne-end-functional arms by RAFT polymerization, which are then "clicked" to an azide functional backbone.[181,182]

- the preparation of a backbone with pendant protected primary amine functionality by RAFT polymerization, which is then deprotected and "armed" by active ester chemistry.[183]

Surface-initiated RAFT polymerization (SI-RAFT)

A variety of processes for surface-initiated RAFT polymerization (SI-RAFT) have been described.[184–186] Often a preliminary step in SI-RAFT involves some chemical transformation to attach RAFT agent functionality to the surface. Another method involves forming radicals on the surface, *e.g.*, by irradiation or through attached initiator functionality, and initiating RAFT polymerization in the presence of a 'free' RAFT agent that becomes surface-bound as a consequence of RAFT polymerization.

Some examples of forming polymer bushes on two-dimensional surfaces by surface-initiated RAFT polymerization include the following.

- Z-connected RAFT agent: BA from silicon wafer.[132] 4VP from ZnO nanoparticles.[187]
- R-connected RAFT agent: MMA from stainless steel.[188] HEMA,[189] CMS,[190] or DMAPMAm[191] from silicon wafer. NIPAm from glass.[192,193] POSS-MA/DMAEMA from poly(dimethylsiloxane).[194] SBEMA from cellulose.[195] VPBA[196] or SDPP[197] from a P(St-*co*-DVB) monolith. MAA from polypropylene.[198] HPMAm from carbon nanotubes.[199] St from clay nanoparticles.[200] Am[201] or St[202] from iron oxide nanoparticles. HEMA from silica nanoparticles.[203]

R-connected strategies are the most popular and are more suited for applications that require permanent surface modification. The Z-connected approach affords a coating that is readily cleaved from the surface using "end-group" transformation/removal techniques.

Strategies for attaching the RAFT agent to the surface vary. Sacrificial RAFT agents are often used and generally necessary to provide good control over graft length and dispersity. In SI-RAFT, the RAFT process can become diffusion controlled. This problem can be alleviated by the presence of low molar mass RAFT agent in the polymerization medium. The approach making use of sacrificial RAFT agents will necessarily produce a linear polymer derived from the sacrificial RAFT agent as a by-product. This, being of low molar mass, is usually readily separated. The sacrificial RAFT agent strategy is useful when grafts of a defined length are required and essential when these are of low molar mass. The graft-length obtained in such experiments is defined largely by the concentration of the sacrificial RAFT agent. For example, in grafting VPBA[196] or SDPP[197] from a P(St-*co*-DVB) porous monolith, it was necessary to form very short graft (5–10 units) to avoid clogging the pores.

Various groups have modelled surface-initiated RAFT polymerization for both Z-connected[204] and R-connected RAFT agents[205] with a view to better defining termination processes and their influence on the efficiency of the process. Zhou *et al.*[206] have recently reviewed processes for surface-initiated RDRP with a focus on biomaterials.

Network polymer synthesis

There has been a recent increase in publications on polymer networks formed by RAFT polymerization in line with the growth in applications of stimuli-responsive systems such as dynamic covalent polymers (see *Self-healing polymers*), porous polymer monoliths or gels (used as chromatographic media,[207–210] flow reactors,[196,197,211] controlled release media,[212] drug delivery vehicles and molecular imprinting[207,208,213,214]) and coatings.[215] RAFT crosslinking polymerization to form network polymers has recently been reviewed.[216]

It might be naively anticipated, that in applying RAFT to network synthesis, that just as RAFT provides control over molecular weight and molecular weight distribution for linear polymers, it would allow control over the distance between crosslinks and thence of pore size in RAFT-synthesized polymer networks. However, controlling the distance between crosslinks in crosslinking (co)polymerization is more akin to controlling monomer sequence distribution during linear polymer formation; a target that remains elusive in the field RAFT[91,92] and RDRP generally.[217]

The development of network structure for two forms of RAFT agent: (a) mono-RAFT agents, $R{-}SC(=S)Z$, and (b) symmetrical trithiocarbonates (these are 'Z'-connected bis-RAFT agents, $R{-}SC(=S)[Z'C(=S)]_n{-}S{-}R$ with $n = 0$) are shown in Fig. 5.[216] The first provides a network with pendant RAFT functionality, the second a network with internal trithiocarbonate linkages.

Covalently crosslinked networks are an important class of stimuli-responsive materials. Often these take the form of swollen gels, commonly hydrogels, which respond to stimuli such as a change in pH, temperature or ionic strength to trigger a change in equilibrium degree of swelling. Polymer networks also find a role in molecular imprinting, monoliths

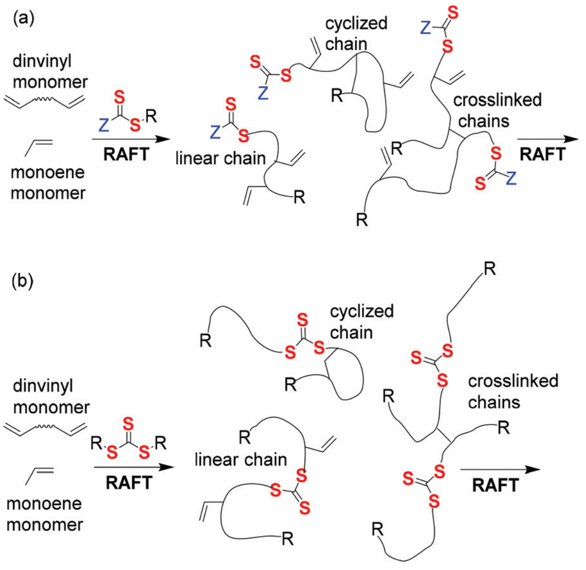


Fig. 5 Structure of "sol" formed with two types of RAFT agent: (a) monofunctional, $R{-}SC(=S)Z$ (b) difunctional, $R{-}SC(=S){-}S{-}R$.

for chromatography or flow chemistry[196,197] and in self-healing polymers or covalent adaptable networks (CAN) based on reversible crosslinks.[218–222]

RAFT polymerization induced self-assembly

Self-assembly of polymers has traditionally involved two steps: (i) dissolution and (ii) microphase separation. The latter step is driven by some change in solvent properties, *e.g.*, by adding a non-solvent, evaporating some solvent or changing the temperature.

A now common approach to forming nano-objects, by block copolymer self-assembly based on RAFT or other RDRP, involves chain-extending a polymer with a second monomer in a solvent chosen such that it is a good solvent for the monomer but a poor solvent for the growing second block, which gradually becomes insoluble. There are, however, many cases where some form of supramolecular order develops as a consequence of polymerization that may also be considered RAFT polymerization-induced self-assembly (PISA), and which are relevant in the context of preparing stimuli-responsive materials.[223]

For example:[224]

- the initialization step in *ab initio* emulsion and some other forms of heterogeneous polymerization.
- the formation of micelles and other structures when forming amphiphilic copolymers by homogeneous RAFT polymerization.
- the formation of micro- or nanogels by RAFT crosslinking polymerization (*e.g.*, core synthesis for core-first stars).[225]
- the formation of stars and other structures by crosslinking polymerization mediated by a macroRAFT agent (*e.g.*, arm-first star synthesis).

RAFT (co)polymerization of functional monomers and the "grafting through" approach to stimuli-responsive polymers

In the design and synthesis of stimuli-responsive polymers the major role of RAFT polymerization is simply as a tool for the construction of well-defined low dispersity polymers from monomers or macromonomers containing appropriate functionality. These processes can be considered examples of the "grafting through" approach of introducing functionality.

As discussed above, most monomers are compatible with RAFT polymerization in unprotected form. However, selection of polymerization conditions to provide appropriate solubility/compatibility for all of the RAFT agent, the monomer(s) and their polymer(s), particularly in the case of amphiphilic copolymers, is often a challenge and can by itself dictate a need for protection strategies.

In the following sections we will briefly consider thermo-, pH-, redox- and light- and chemical-responsive polymers which are prepared by (co)polymerization of monomers already mentioned in Monomers in RAFT polymerization. We will then discuss RAFT polymerization of several monomers classes that have assumed a special role in the synthesis of stimuli-responsive polymers, in particular, betaine (or zwitterionic) monomers, ionic liquid monomers and metallo- (or metal chelating) monomers. Finally we will consider the synthesis of polymers based on monomers designed for post-polymerization modification. A big advantage of the post-polymerization modification processes is that they enable libraries of polymers to be prepared from a common precursor.

Thermo-responsive polymers

In the present context, the term "thermoresponsive" generally relates to the solution properties of polymers that display either a lower critical solution temperature (LCST) such that they phase separate from aqueous solution upon heating, or to polymers with an upper critical solution temperature (UCST), which phase separate from solution upon cooling. Most reviews on the subject have a strong focus on materials displaying LCST behaviour.[226,227] A relative few detail UCST behaviour.[228] Aqueous LCST or UCST values must normally be within the temperature range 10–100 °C to attract interest.

The best known examples of RAFT-synthesized polymers showing LCST behaviour are P(NIPAm) and P(OEGMA).[226,229] LCST behaviour is also displayed by many other acrylamide and methacrylamide homo- and copolymers.[226] The respective monomers present no difficulty in RAFT polymerization. Other polymers to show LCST behaviour include poly(vinyl alcohol) copolymers [formed from P(VAc)],[230] P(VCL),[231] P(DAEMA)[232] and some polymer ionic liquids (see below).[233,234] RAFT-synthesized polymers showing UCST behaviour include some based on zwitterionic betaine monomers (see below). LCST values can be tuned with the synthesis of copolymers (block, gradient), by controlling the polymer architecture (stars), even by changing the end groups.[235]

Much interest lies in materials (blocks, biopolymer conjugates, particles, surfaces) that contain segments showing thermoresponsive behaviour where such behaviour may provide a trigger for therapeutic release.

pH-Responsive polymers

Polymers that are pH-responsive display a change in solubility or conformational properties as a function of the acidity of the medium.[236–238] These polymers commonly possess ionizable groups that are pendant to the backbone, *e.g.*, tertiary amino in P(DMAEMA) or pyridyl in P(4VP), which are cationic at lower pH, or carboxy in P(AA), which is anionic at higher pH. Other ionisable pH-responsive polymers are based on amino acid-derived acrylamides[239,240] and methacryloyl sulphonamides (**47**) (Table 5).[241]

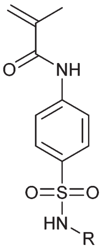
Incorporation of acidic or basic comonomers into polymers which show LCST behaviour paves the way for using a pH change to shift the LCST.[242]

Another class of pH-responsive polymers, not considered here, are those that undergo an irreversible pH-induced chemical transformation.[236]

Redox-responsive polymers

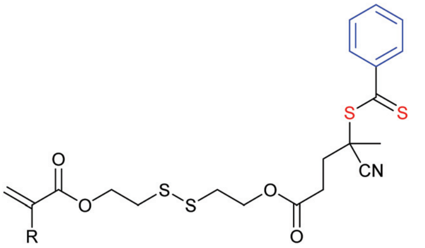
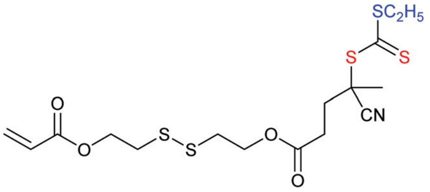
Redox responsive polymers for biomedical applications have been reviewed.[245] An important class of redox-responsive com-

Table 5 Examples of RAFT-synthesized pH responsive polymers

Monomers	RAFT agent	Comment	Ref.
Tertiary amino methacrylate[a]	6	PEG block copolymers	243
DMAEMA/MMA	2	Compared with DMAEA/MA	244
DMAEA/MA	29	Compared with DMAMEA/MMA	244
 47	6 15	Polymer pK_a ~4.5–7.5 dependent on R. Water soluble in ionized form	241

[a] 2-(Diisopropylamino)ethyl methacrylate, 2-(piperidin-1-yl)ethyl methacrylate, 2-(dibutylamino)ethyl methacrylate.

Table 6 RAFT disulphide monomers used in-synthesis of redox-responsive polymers

RAFT disulfide monomer	Comment	Ref.
	R = CH_3 R = H	250 251–253
		246

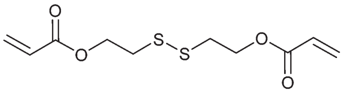
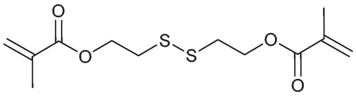
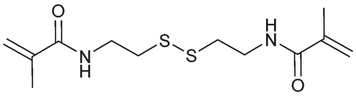
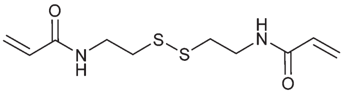
prises the metallopolymers, which are described separately below.

A second major class of RAFT-synthesized redox-responsive polymers are those that contain disulfide linkages[149,246–249] that can be reversibly cleaved by reduction. This includes microgel, hyperbranched or star polymer formed by self-condensing vinyl polymerization (Table 6) or RAFT crosslinking polymerization (Table 7).

Photo- or light-responsive polymers

There are a wide variety of materials that can be considered within the category of light or photo-responsive polymers. The light responsive functionality can be introduced into the RAFT-synthesized polymer through functionality the monomer (Table 8),[277] the RAFT agent (Table 9)[278] or by post-polymerization functionalization.[279] These polymers fall into a number of, not mutually exclusive, classes, which include photochromic polymers, certain electroactive polymers and light-harvesting polymers.

Table 7 Crosslinking monomers containing disulphide linkages used in-RAFT-synthesis of redox-responsive polymers

Crosslinking monomer	Comment	Ref.
	Nanogels Arm-first nanogels	254 and 255 256–259
	MMA nanogels DMAEMA nanogels Arm 1st star nanogels Branched polymer as precursor to thiol-functional polymer	260–262 263 161 and 264 265
	Arm 1st star nanogels	266
	Arm 1st star nanogels Core first star nanogels Nanogels	159 and 267–271 149 272–276

Other light-responsive polymers that are not considered within the scope this review, since the changes induced are most often irreversible, include photo-scissionable polymers, which undergo main-chain[280] or side chain photocleavage,[20] photo-crosslinkable polymers, which contain various photo-initiator functionality to achieve photo-crosslinking,[281] and polymers for photo-lithography, which are typically pH sensitive polymers containing a photo-acid generator.[282]

In forming light responsive polymers it is important to consider the properties of the thiocarbonylthio group which is itself photoactive and can, *e.g.*, quench florescence or photo-dissociate, necessitating end group removal.[283]

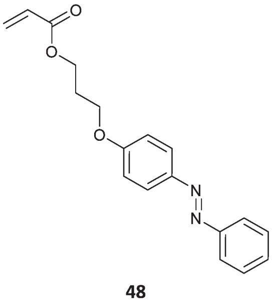
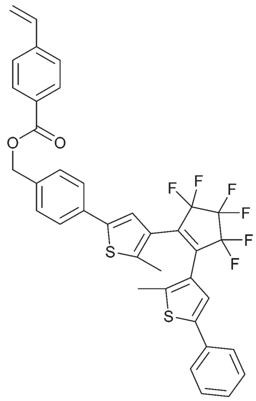
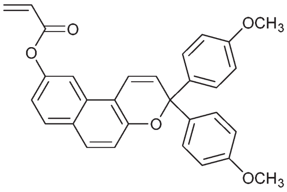
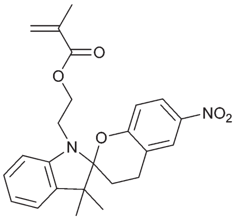
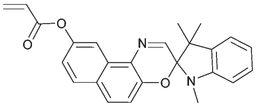
Photochromic polymers. Photochromic polymers contain functionality that can undergo some form of, preferably reversible, light-induced isomerization to change colour or light absorption characteristics.[284–289]

Often there is an associated change in the hydrophilic–hydrophobic balance or more generally the solvophilic-solvophobic balance for the material so as to change solubility. This can be used cause light-induced self-assembly/disassembly, or otherwise modify polymer properties.[290] This response can also be used a trigger mechanism for the delivery of therapeutics.

RAFT-synthesized tails on matrix encapsulated photochromic dyes provide a method of tuning the dye switching speed.[284]

Light harvesting polymers. There are now many examples of RAFT-synthesis of light harvesting polymers.[133–136,291–300] For example, Chen *et al.* prepared polymers comprising a RAFT-synthesized P(CMS) backbone (prepared with **5**), which was then functionalized by Huisgen cycloaddition to have pendant oligomeric π-conjugated chromophores.[299]

Table 8 Monomers for synthesis of light-responsive polymers

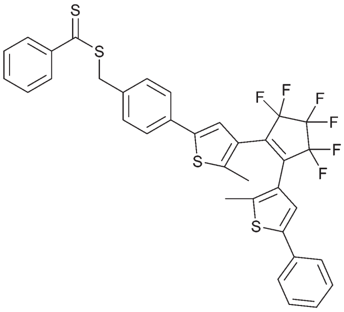
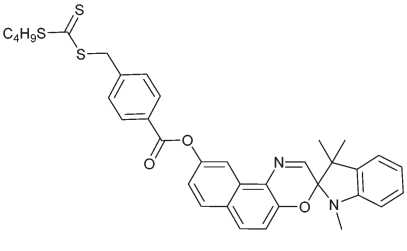
Photochromic monomer	Polymerization[a]/comment
 **48**	**48** (**2**)[277] Light induced self-assembly, gold nanoparticles
 **49**	SI-RAFT[287] Photochromic particles
 **50**[b]	**50**-*co*-MMA (**2**)[285] **50**-*co*-MA (**2**)[285] MMA-*b*-**50**-*co*-MA (**2**)[285] MMA-*b*-**50**-*co*-MA (**2**)[286] Photochromic statistical and block copolymers
 **51**	**51**-*co*-4VP (**6**)[301] Photochromic nanowires prepared by electrospinning
 **52**	NAM-*b*-(**52**-*co*-NIPAm) (**35**)[302]

[a] Polymerizations shown as: monomer(s) (RAFT agent)[ref]. [b] Other naphthopyran monomers also described.[285]

Chemical-responsive polymers

In the present context chemical-responsive polymers show a reversible change in the presence of reagents, which can be introduced to or removed from the system. These reagents include gases such as O_2,[304] CO_2 and NO.

Table 9 RAFT agents for synthesis of light-responsive polymers

Photochromic RAFT agent	Polymer/comment
	P(NIPAm)[303] Thermo-responsive gold nanoparticles
	P(St)-*b*-P(BA)[284] P(BA)-*b*-P(St)[284] P(NIPAm)-*b*-P(NAM)[302] Control of photochromic switching speed

Carbon dioxide-responsive polymers. CO_2 responsive polymers can also be considered a sub-class of pH responsive polymers. They find application in various fields,[305–307] which include CO_2-capture and storage, in CO_2 switchable surfactants and in polymersomes with CO_2 triggered release.

The most common CO_2 responsive monomers are those possessing basic amine, amidine or guanidine functionality.[306] These groups react with the carbonic acid formed when CO_2 dissolves in water to form the respective ammonium, amidinium or guanidinium bicarbonate salts.

Thus, RAFT-synthesized P(DMAEMA)-*block*-P(DMA) copolymers have been developed as the basis for CO_2-breathing vesicles.[308] Dual CO_2–O_2 responsive P(DEAEMA/PFS) microgels with have been prepared by RAFT crosslinking-copolymerization.[309]

Other polymers shown to be both CO_2- and pH-responsive include the methacryloyl sulphonamides.[241] These polymers are notable for having pK_as in a biologically relevant range (pH = 4.5–7.4).

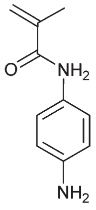
In that nucleophilic groups may react with the thiocarbonylthio RAFT agent functionality, polymers are often formed by post-polymerization modification, *e.g.*, using active ester chemistry.[310]

Nitric oxide responsive polymers. The monomer **53** (Table 10), and derived polymers, react with NO in aqueous solution in the presence of O_2 to generate light-sensitive phenyldiazonium groups.[19]

The dithiobenzoate RAFT end of the low dispersity PEG-*b*-P(NIPAm-*co*-**53**) was apparently stable in the presence of the primary aromatic amine.[19]

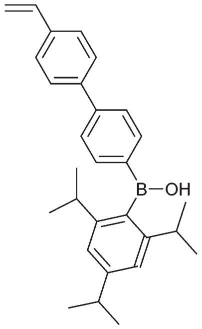
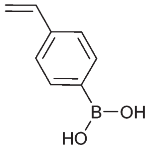
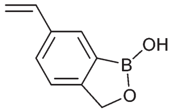
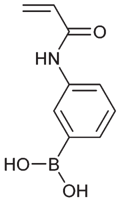
Other chemical-responsive polymers. A wide range of polymers have been prepared with functionalities designed to invoke a specific response. These include polymers containing monomer units with, *e.g.*, boronic acid (Table 11, see also

Table 10 RAFT-synthesis of NO-responsive polymers

NO-responsive monomer	Polymerization[a]
 **53**	PEG-*b*-(NIPAm-*co*-**53**) (**8**)[19]

[a] Polymerization shown as: monomer(s) (RAFT agent)$^{\text{ref}}$.

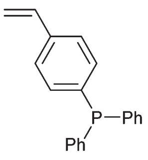
Table 11 Boronic acid monomers

monomer	RAFT agent	Comment	Ref.
	**24**	Fluoride ion responsive polymers	316
 VPBA	(**20**)[a]	Monomer used in SI-RAFT monolith functionalization. Monolith for catalyst in flow chemistry	196
	**25**	Sugar responsive polymers	317 and 318
	(**24**)[a]	Sugar responsive polymers	319 and 320
		Monomer used in SI-RAFT to form affinity column	321

[a] Surface-bound RAFT agent based on the RAFT agent indicated.

Brooks *et al.*[311]) or phosphine functionality (*e.g.*, DPPS, Table 12) and glycopolymers (Table 13). Other materials that might be considered here are (typically crosslinked) polymers prepared with molecular imprinting.[210] Applications include fluorescent or colorimetric sensors[312] and stationary phases for chromatography.

Table 12 Phosphine monomers

Monomer	RAFT agent	Comment	Ref.
 DPPS	(**20**)[a]	Monomer used in SI-RAFT monolith functionalization. Monolith for catalyst in flow chemistry	196
	30	DPPS-*co*-St potential use in forming catalysts	322
	6	DPPS-*co*-(alkylstyrene) potential use in forming catalysts	323
	(**6**)[b]	DPPS-*co*-St block used as arm macro RAFT agent in forming nanoreactor by crosslinking polymerization	324

[a] Surface-bound RAFT agent based on the RAFT agent **20**. [b] PEGMA-*co*-MAA macro RAFT agent formed with **6**.

Glycopolymers possess an all carbon backbone and have pendant oligosaccharide groups. They are usually derived by polymerization of acrylic, styrenic or vinyl glycomonomers. The polymers have attracted widespread attention for various biological and biomedical uses with expectation that the polymers might mimic analogous polysaccharides in terms of engendering a bioresponse.[313]

In that it can carried out in homogeneous aqueous media, at moderate to ambient temperature, with monomers carrying complex functional groups, RAFT polymerization is particularly well-adapted to the synthesis of glycopolymers. Ghadban and Albertin[313] have comprehensively reviewed the synthesis of glycopolymers by various RDRP, including RAFT polymerization (see also ref. 314). RAFT and ATRP are clearly the dominant processes for forming such polymers.[313,314] The immobilization of glycopolymers on surfaces by various processes, including SI-RAFT, has also been recently reviewed.[315]

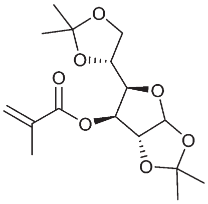
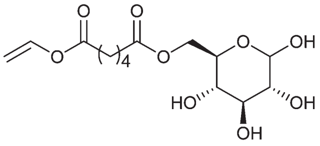
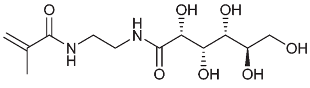
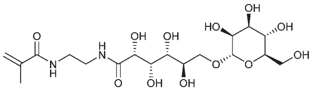
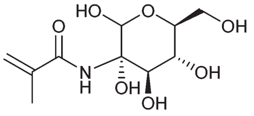
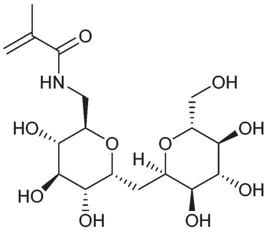
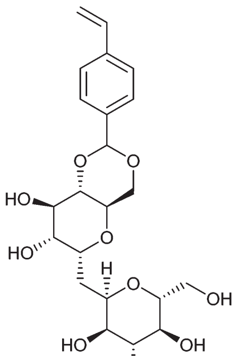
Polymers based on betaine or zwitterionic monomers

Polymers based on carboxybetaine (*e.g.*, CBMMA,[240,335,336] CBEMAm[337]), sulfobetaine (*e.g.*, SBPMAm[338–340] SBPMA[341–343]), and phosphobetaine monomers (*e.g.*, MPC[344–347]) monomers (for additional examples see ref. 339 and 348) often display UCSTs and can show salt ionic strength-responsive behaviour. These polymers are also used in biosensors for their ultra-low fouling characteristics. The betaine monomers can be polymerized directly by RAFT polymerization (Table 14).[349] However, these polymers have also been made by post-polymerization modification of RAFT-synthesized polymers.

A library of sulfobetaine polymers with general structure **61** X = H, CH_3, Y = O, NH, n = 2, m = 3, 4 was prepared using three different synthetic strategies.[343] The (meth)acryates (Y = O) were prepared by direct RAFT polymerization of the sulfobetaine monomers or by modification of P(DMAEMA) with the appropriate sulfone (Scheme 7).

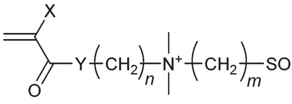
The (meth)acrylamides were prepared by active ester chemistry (Scheme 8). UCST behaviour was found to depend strongly on structure.[343]

Table 13 Glycomonomers

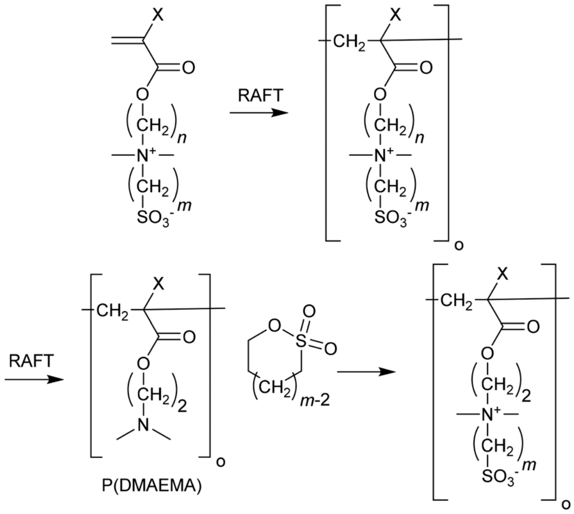
Glycomonomer	Polymerization[a]
 **54**	**91**-*co*-**54** (**24**)[325] **54**-*b*-HEMA-*b*-NIPAM (**6**)[326]
 **55** (glucose-based)	DEGMA-*b*-**55** (**43**/**43H**$^+$)[327] **55**-*co*-NIPAM-*b*-NIPAM (**24**)[328]
 **56**	**56**-*co*-AEMA-*co*-HEAm (**6**)[329]
 **57**	**57**-*co*-AEMA-*co*-HEAm (**6**)[329]
 **58**	**58** (**26**)[259] **58**-*co*-FMA[b] (**5**)[330] **58** (**6**)[331]
 **59** (trehalose-based)	**59**-*b*-AEMA (**16**)[332] PEP-*b*-(**59**-*grad*-DMA)[c] [333]
 **60** (trehalose-based)	**60** (**150**[d])[334]

[a] Polymerizations shown as: monomer(s) (RAFT agent)[ref]. [b] FMA – fluorescein *O*-methacrylate. [c] Poly(ethylene-*alt*-propylene) macroRAFT agent derived from **24**. [d] See Table 34 for structure.

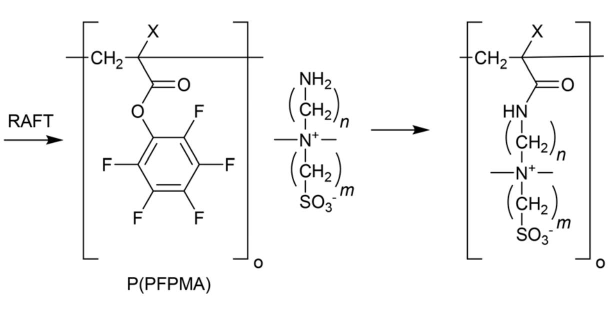
Table 14 RAFT-synthesis of polymers based on betaine monomers

Betaine monomer[a]	Polymerization[b]
CBMMA	CBMMA-*b*-BMA (**6**)[335] CBMMA-*b*-HPMA (**19**)[240] CBMMA-*b*-EHMA (**6**)[336] CBMMA-*co*-HEMA-*co*-MBA (**28**)[c] [350] CBMMA-*co*-DMAEMA (**24**)[256]
CBEMAm	HPMAm (**6**)[337] HPMAm-*b*-CBEMAm (**6**)[337]
SBPMAm	NIPAm-*b*-SBPMAm-*b*-AMBA (**22**)[340] SBPMAm (**6**)[339] SBPMAm-*b*-DMAm (**6**)[339] DMAm-*b*-SBPMAm (**12**)[339] NIPAm-*b*-SBPMAm (**13**)[338]
 **61**	**61** X = CH_3, Y = O, n = 2, m = 3, 4 (**2**)[343] **61** X = H, Y = O, n = 2, m = 4 (**34**)[343]
MPC	BA-*b*-MPC (**33**)[344] MPC-*b*-DEAM (**6**)[346] MPC-*b*-SBEMA (**6**)[346] MPC-*b*-TMAPMAm (**6**)[347] MPC-*b*-AMPS (**6**)[347]

[a] Monomer abbreviation are provided in Fig. 2. [b] Polymerizations shown as: monomer(s) (RAFT agent)[ref]. [c] Hyperbranched polymer.



Scheme 7 Synthetic routes to sulfobetaine (meth)acrylates.



Scheme 8 Synthesis of sulfobetaine methacrylamides by active ester chemistry from P(PFPMA).

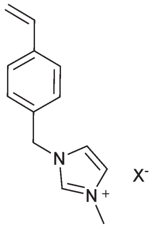
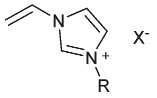
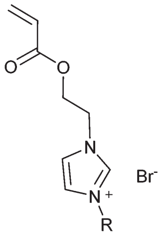
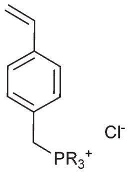
Polymer ionic liquids

The term ionic liquid monomer is often used to embrace monomers comprising permanent ionic functionality whether or not they meet the more generally accepted definition that they exist as a liquid at some temperature below 100 °C. The term polymer ionic liquid is used to refer to polymers that comprise units of an ionic liquid monomer.[351,352] The polymers themselves may not be ionic liquids.

Polymer ionic liquids can be prepared directly by RAFT polymerization of "so-called" ionic liquid monomers (**62–65**, Table 15). Polymer ionic liquids have also been prepared by introduction of the liquid crystal functionality post-polymerization by quaternization of a halo-functional polymer (*e.g.*, P(CMS)[353,354]) or by thiol-ene chemistry.[355]

Most ionic liquid monomers are (meth)acrylate- or styrene-based and dithiobenzoates or trithiocarbonates used to mediate their RAFT polymerization (Table 15). Xanthate RAFT agents (**63**) were used to control polymerization *N*-vinyl imidazolium salts, which are presumed to be LAMs (or IAM).[356]

Table 15 RAFT-synthesis of polymer ionic liquids

Ionic liquid monomer	RAFT agent	Comment	Ref.
 **62**	**24**	$X^- = BF_4^-$ Polymer shows UCST behaviour in methanol/water	233
	21	$X^- = Cl^-$ Nanogels formed by crosslinking polymerization	357
 **63**	(**37**)[a]	$X^- = BF_4^-$, $R = C_2H_5$ Double hydrophilic block from PNIPAm or PDMAm macroRAFT agents	358
	38	$X^- = Br^-$, NTf_2^-, $R = C_2H_5$ Polymer is catalyst for Diels-Alder reaction	359
	38	$X^- = Br^-$, $R = C_4H_9$ NIPAM copolymer shows UCST in CH_3CN	360
	37, 38	$X^- = Br^-$, R = alkyl	356
 **64**	**6**	$R = CH_3$, C_2H_5 Polymer is salt responsive	361
	22	$R = CH_3$, CH_2Ph Polymerization induced self-assembly in forming block copolymer	362
	1	$R = C_4H_9$ Block copolymer with *N*-(thiazol-2-yl)methacrylamide. Magnetic properties of derived metal complexes	363
 **65**	**21**	$R = Ph$, C_4H_9 Nanogels formed by crosslinking polymerization	357

[a] MacroRAFT agent derived from **37**.

The polymer ionic liquids display a range of stimuli-responsive behaviours dependant on the particular structures and conditions (*e.g.*, Table 15).

Self-healing polymers

Various groups have described self-healing polymers or stress relieving polymers. These polymers are networks that comprise a fraction of dynamic bonds, which may take the form of non-covalent supramolecular interactions or dynamic covalent bonds. These bonds allow the polymers able adapt their structures in response to external stimuli which may take the form of heat, UV irradiation or mechanical stress.

In some case the dynamic bonds involve a trithiocarbonate group and the dynamic process is UV or thermally stimulated RAFT.[221,222,364–367] In other cases RAFT is simply a tool to construct functional copolymers and the dynamic process is acylhydrazone formation,[368–370] imine formation,[371–373] Diels Alder reaction,[374] boronic acid ester formation,[375,376] metal complex formation[377] or (multiple) hydrogen bond formation.[378]

Metallopolymers

Many have studied the incorporation of metal complexes into polymers to provide materials that combine the catalytic, magnetic, and/or electronic properties of metal complexes with the desirable mechanical and processing properties of the host polymers.[379–381] This section relates to RAFT polymerization of monomers that incorporate a metal complex (Table 16) or possess metal chelating group (Table 17) as pendant functionality. The section is, in part, an update to that embraced in the review of optoelectronic polymers published in 2011.[283] Metallopolymers formed by RDRP methods, including RAFT, and other forms of living or controlled polymerization have also been reviewed by Whittell *et al.* in 2011[379] and by Hardy *et al.* in 2014.[380]

RAFT polymerization making use of metal containing RAFT agents[139] or metallopolymer macroRAFT agents[382] have also been described (Table 18, for additional examples see previous review[283]).

Electroactive polymers

Organic semiconductors. The synthesis of polymers with an organic semiconductor moiety either as a block or as pendant group to the backbone. We also consider polymers with attached dyes for use in light-harvesting, photochromic and some imaging applications under Light responsive polymers above.

Polymers containing thiophene and other conjugated rings such as part of the backbone are not directly available by radical polymerization except in special circumstances. For example, RAFT Ring-opening polymerization provides a route to a rod-polymer with in-chain acene (anthracene) functionality (Scheme 9).[396] It is, however, possible to efficiently convert preformed conjugated polymers to macroRAFT agents.

Table 16 Metallopolymers

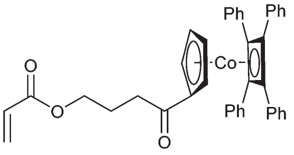
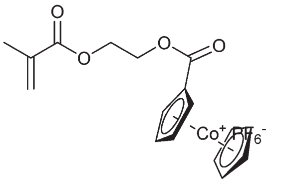
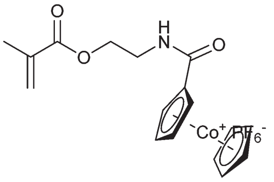
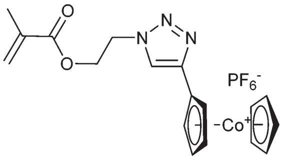
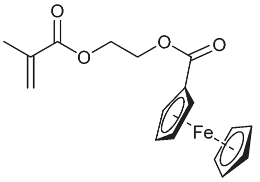
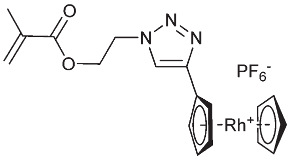
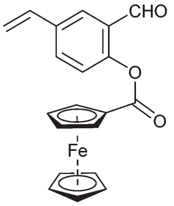
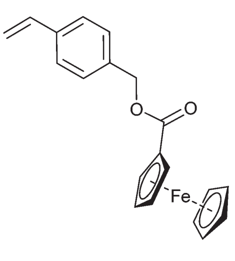
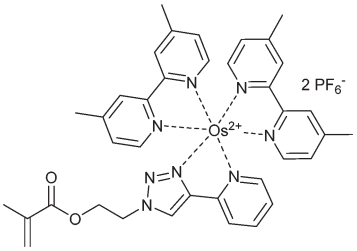
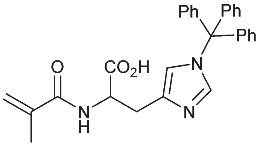
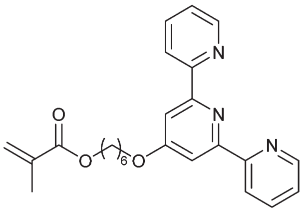
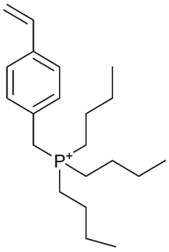
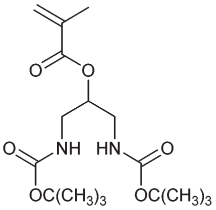
Metallomonomer	RAFT agent/ comment	Ref.
 **66**	**24, 32** Loss of control for homopolymer, low dispersity for copolymer with MA and copolymer blocks	383–385
 **67**	**1** Low dispersity homopolymer, block copolymers	386, 387
	**1** Low dispersity homopolymer, block copolymers	386, 387
	**1** Low dispersity homopolymer, block copolymers	386–388
	**9** Block copolymer with macroRAFT formed from cobaltocenium monomer (**67**)	387
	**1** Low dispersity homopolymer for conversion <50%	389
	**2, 25** MacroRAFT used in block synthesis Self-assembly of PEO block	390, 391
	**17** Triblock copolymer prepared to make responsive vesicles	392
	**2** Light harvesting copolymer	298

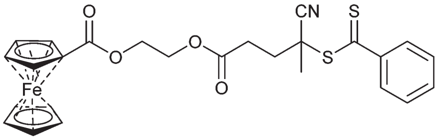
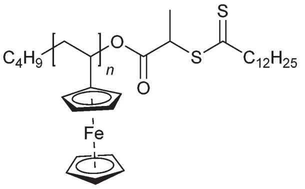
Table 17 Metal chelating polymers

Metal chelating monomer	Polymerization[a]/comment
 **68**	**68**-*co*-BMA (**2**)[393] **68**-*co*-LMA (**2**)[393] Self-healing network formed by cross-linking copolymer with Zn^{2+}
 **69**	**69**-*co*-MMA (**2**)[377] **69**-*co*-BMA (**2**)[377] **69**-*co*-LMA (**2**)[377] Self-healing network formed by cross-linking copolymer with Cd^{2+}
 **70**	(**66**-*co*-MMA)-*b*-**70**(**32**)[385] Precursor to gold-containing block copolymer
 **71**	**71**-*co*-HPMAm (**149**)[394] Used in forming platinum drug

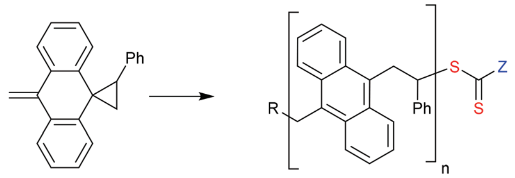
[a] Polymerizations shown as: monomer(s) (RAFT agent)[ref].

Poly(3-hexylthiophene) (P3HT) macroRAFT agents are summarized in Table 19. MacroRAFT agents **72–74** possess a P3HT moiety as the Z group. A potential disadvantage is that the P3HT can be readily cleaved from the RAFT-synthesized polymer. On the other hand, macroRAFT agents **75–80** possess P3HT as the R group and thus possess a relatively stable block

Table 18 Metallo-RAFT agents

RAFT agent	Monomer[a]/ref.
	OEGMA[395]
	DEAm[382]

[a] Monomer polymerized.



Scheme 9 Example of RAFT ring-opening polymerization (R = PhCH$_2$, Z = Ph or *N*-pyrrole).

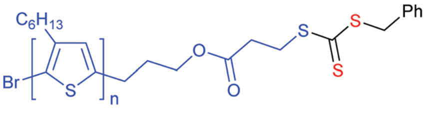
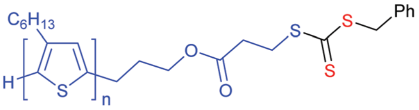
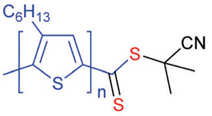
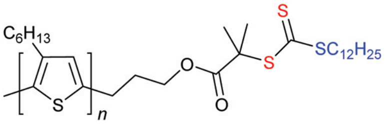
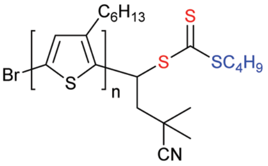
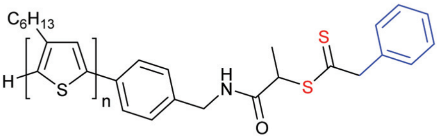
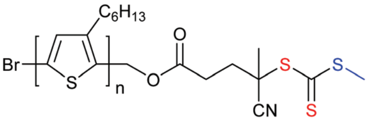
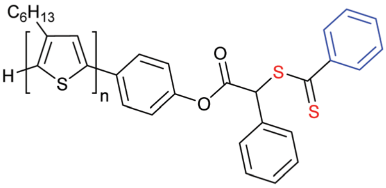
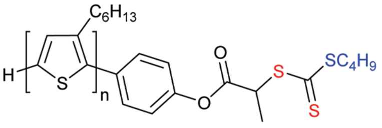
linkage allowing the RAFT ZCS$_2$ to be removed or transformed keeping the block structure intact. P3HT may also be introduced post-RAFT polymerization as a block[397] or a pendant functionality.[398]

Earlier, pre-2011, studies on grafting from/to electroactive graphitic nanoparticles (graphene, carbon nanotubes) and fullerene are documented in our review.[283] There are also more recent reviews that embrace this topic.[399] Fullerene containing polymers have been prepared by RAFT polymerization and various strategies have been used in incorporate the fullerene functionality. Most recent studies involve polymer modification post-RAFT polymerization to introduce the fullerene moiety as a pendant group,[400–404] as an end group[405] or as some form of supramolecular assembly (Table 20).[406]

Modification of RAFT-synthesized polymers

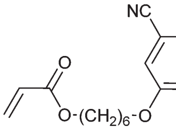
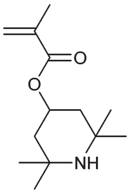
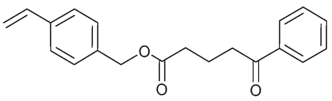
The installation of functionality into appropriately reactive, RAFT-synthesized precursor polymers provides a versatile method for forming stimuli-responsive polymers. The procedure then requires the preparation of a polymer containing monomer units suitable for efficient modification, to introduce the groups of interest. An advantage of this methodology is that libraries of polymers are then available that differ only in the type of introduced functionality; all have the same backbone structure. The application of this strategy in the context of thermoresponsive polymers has been reviewed by Roth.[420] A second advantage is the provision of polymers with functionality that might interfere with radical polymerization or with the RAFT process if a more direct grafting through route was employed. One of the more important applications of this technology is in the synthesis of polymer-drug conjugates. However, there are many other applications.

Table 19 Poly(3-hexylthiophene) (P3HT) macroRAFT agents

P3HT macroRAFT agent	Monomer[a]/ref.
 **72**	St[407,408] 4VP[409]
 **73**	Copolymer[410]
 **74**	MMA[411]
 **75**	St[412]
 **76**	St[413]
 **77**	[b] 414
 **78**	St[413]
 **79**	[b] 415
 **80**	2VP[416]

[a] Monomer polymerized. [b] Use of macroRAFT agent in RAFT polymerization not reported.

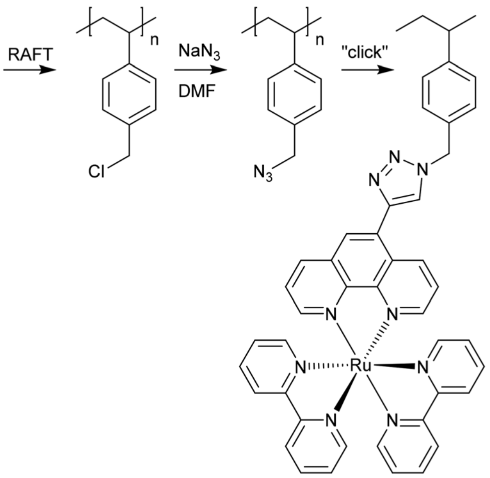
Table 20 Monomers for organic semiconductors

Monomer	Polymerization[a]/comment
 **81**	**81** (**5**)[417,418] Precursor to phthalocyanine dye
 **82**	**82** (**1**)[419] Precursor to transparent conducting polymer
 **83**	**83**-*co*-St (**36**)[402] Precursor to fullerene functional polymer

[a] Polymerizations shown as: monomer(s) (RAFT agent)$^{\text{ref}}$.

It is possible to use conventional chemistry for polymer modification either to directly introduce a desired functionalities. For example,

- esterification of polymers with hydroxyl functionality, *e.g.*, P(VA) and VA copolymers (P(VA) from RAFT-synthesized P(VAc))[230] or HEMA copolymers,[421] making use of *N*,*N*-dicyclohexyl carbodiimide (DCC) coupling.
- halogen substitution. There are many examples of modification of RAFT-synthesized halogen-functional polymers, *e.g.*, of P(CMS) and post-functionalisation by quaternization with a tertiary amine[422] or a phosphine,[79,423] by reaction with a phosphonate,[424] potassium phthalimide,[401] use in a Williamson ether synthesis,[323] or conversion to an azide (Scheme 10);[297] of poly[(4-bromophenyl)(vinyl)sulphane] [P(BPVS)] by Buchwald–Hartwig amination[425,426] or Suzuki coupling;[425,426] of poly(bromoethyl acrylate) – a variety of processes have been described by Barlow *et al.*[427]



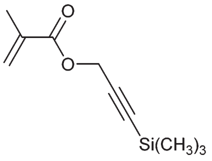
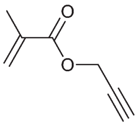
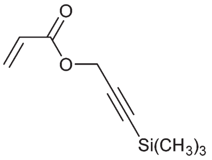
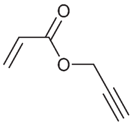
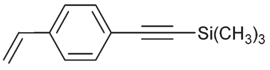
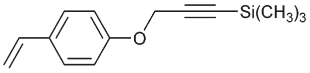
Scheme 10 Synthesis of metallopolymer from RAFT-synthesized P(CMS) by click chemistry.

However, a common approach is to introduce appropriate groups for subsequent transformation by what are often called "click" processes, though the quality of the "click" reactions is in some cases questionable.[428] In this context, we consider the RAFT polymerization of monomers for azide–alkyne 1,3-dipolar (Huisgen) cycloaddition, monomers containing active ester groups, monomers with latent amino- or thiol-functionality, and monomers with isocyanate or isothiocyanate groups.

Monomers for azide–alkyne dipolar cycloaddition. Many papers have been published concerning the combination of RAFT and azide–alkyne 1,3-dipolar cycloaddition.

Some alkyne-functional monomers and the polymers formed with them by RAFT polymerization are listed in Table 21. In most cases monomers with protected alkyne functionality have been used since the alkyne group is susceptible

Table 21 Alkyne-functional monomers used in RAFT (co) polymerization

Monomer	Polymerization[a]
 **84**	**84**-*b*-PEGMA (**1**)[435] **84**-*co*-MMA-*b*-St (**2**)[436] **84** (**2**)[429] **84**-*co*-MMA (**4**)[437] **84**-*co*-MMA (**6**)[438] **84**-*co*-PEGMA (**2**)[439] **84**-*b*-PEGMA (**2**)[439] **84**-*b*-PEGMA (**6**)[440] Methacrylate multi-block (**8**)[441] Methacrylate multi-block (**6**)[442]
 **85**	PEGMA-*b*-**85** (6)[443] [85 (2)[429]][b]
 **86**	**86**-*co*-EGDMA (**27**)[444] Acrylate multi-block (**33**)[445] Acrylate multi-block (**24**)[446]
 **87**	**87**-*co*-PEGA (**24**)[447] **87**-*co*-AA (**31**)[448–450] **87**-*co*-NAS-*co*-NIPAM (**31**)[451]
 **88**	**88**-*b*-St (**30**)[452,453] PTHPA-*b*-88-*co*-St (9)[454]
 **89**	**89**-*co*-4VP-*b*-St (**24**)[436] St-*b*-**89**[455] **89** (**30**)[456]

[a] For the case of block copolymer the monomers are listed in the sequence they were used. Polymerizations shown as: monomer(s) (RAFT agent)$^{\text{ref}}$. [b] Side-reactions were observed.

to reaction with radicals. It was observed that homopolymerization of **85** gave an insoluble (crosslinked) product.[429] However, no issues were reported in the case of the copolymerizations reported in Table 21.

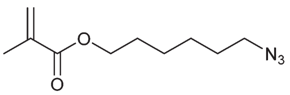
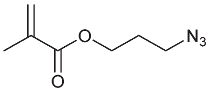
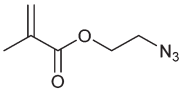
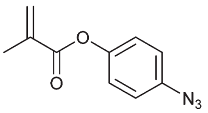
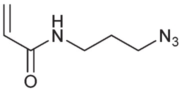
Azides also may undergo side reactions under polymerization conditions. In particular, azides are known to undergo 1,3-dipolar cycloaddition with electron deficient monomers, such as methacrylates.[430] However, these issues and appear to be largely mitigated by conducting polymerization at near ambient temperature or below.[431,432] Azide functional monomers that have been exploited in RAFT polymerization are listed in Table 22. Azide functionality is often incorporated post-RAFT polymerization,[297,433,434] *e.g.*, poly(4-vinylbenzyl azide) was prepared by reaction of P(CMS) with sodium azide in DMF in high yield (Scheme 10).[297]

Monomers with "ene" or diene functionality. The Diels–Alder or hetero-Diels Alder reaction can be an efficient process for polymer modification or assembly. Ene-functionality is also used as a thiol-reactive functionality.

Even though it seems possible to introduce certain diene functionality (Table 23) by direct RAFT polymerization of the appropriate monomers, the same diene groups can also be produced by post-polymerization modification (*e.g.*, 2,4-pentadieneyl,[464] furfuryl[465]).

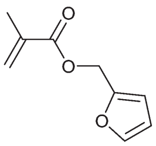
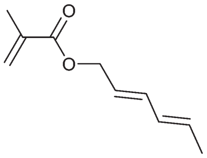
Allyl functionality reacts only very slowly under conditions required to polymerize methacrylates or styrenes and can be incorporated directly by copolymerization of the appropriate monomers (*e.g.*, AMA) to give a low dispersity polymer (Table 24). With more reactive propagating species, *e.g.*, in AN/AMA copolymerization, it is clear that the allyl functionality is not unreactive such that hyperbranched polymers are formed even a modest monomer conversions.[466]

Table 22 Azide functional monomers used in RAFT (co)polymerization

Monomer	Polymerization[a,b]
 **90**	**90** (S28)[457,458] **90** (S6)[459,460] **90**-*co*-MMA (**6**)[404]
 **91**	**91** (**17**)[461] **91**-*co*-St (**24**)[325] **91**-*co*-**54** (**24**)[325]
 **92**	**92**-*b*-MMA (**10**)[431]
 **93**	**93**-*co*-MA (**25**)[462] **93**-*co*-MMA (**2**)[432] **93**-*co*-MA (**41**)[432,462] **93**-*co*-St (**41**)[432]
 **94**	DMA-*b*-(**94**-*co*-NIPAm)(**6**)[463]

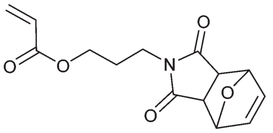
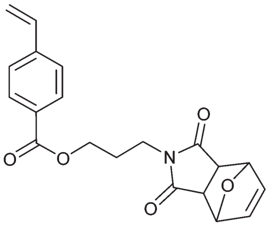
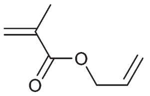
[a] Polymerizations shown as: monomer(s) (RAFT agent)[ref]. [b] The suffix S before the RAFT agent indicates a surface initiated RAFT polymerization.

Table 23 Monomers with diene functionality used in RAFT (co) polymerization

Monomer	Polymerization[a]
 **95**	**95** (**17**)[468] **95**-*b*-PEGMA (**17**)[469] **95**-*b*-BMA (**17**)[374] OEGMA-*b*-**95** (**18**)[470]
 **96**	**95**-*co*-St (**21**)[471]

[a] Polymerizations shown as: monomer(s) (RAFT agent)[ref].

Table 24 Monomers with ene or protected ene functionality used in RAFT (co)polymerization

Monomer	Polymerization[a]
 **97**	**97**-*co*-PEGA (**23**[b])[472]
 **98**	**98**-*co*-St (**24**)[473] **98**-*co*-**107** (**24**)[473]
 AMA	DMAm-*b*-AMA (**24**[c])[474] AMA SIP with xanthate[475]

[a] Polymerizations shown as: monomer(s) (RAFT agent)[ref]. [b] Dopamine-Functional RAFT agent derived from **23**.[476] [c] Bis-RAFT agent derived from bis(hydroxyethyloxypropyl)polydimethylsiloxane and **24**.[474]

Maleimide "ene"-functionality always needs protection during RAFT polymerization, which can be achieved by forming a Diels–Alder adduct, (Table 24). The maleimide functionality is regenerated by heating the product at >110 °C. However, in unpublished work, we have found that the rate of retro Diels–Alder reaction for furan-maleimide adducts may also be significant at commonly used polymerization temperatures (*e.g.*, 60 °C) and is of particular concern when longer polymerization times are used (*e.g.*, 24 h).[467]

Monomers for active ester chemistry. A variety of active esters monomers have been used in RAFT polymerization. Some recent examples of (co)polymers are shown in Table 25. For pre-2012 examples consult our previous reviews.[29–32]

A major application has been the synthesis of biopolymer conjugates. However, many other stimuli-responsive polymers have also been targeted (*e.g.*, dual thermos- and photo-responsive polymers[477]).

Monomers with latent amino- or thiol-functionality. Monomers containing primary or secondary amino or thiol-groups are not easily amenable to RAFT polymerization. However, this functionality can be present in protected form, *e.g.*, the pyridyldisulfide in **110–112** and the thioacetyl group of **113** are protected thiol-groups, and the *t*BOC-group in monomers **114–117** and the phthalimido group of **118** are protected primary amine-groups (Table 26).

Simple protonation has been shown to provide protection for primary amino-functional monomers. Thus (co)polymerizations of AEMA,[502–507] AEAm,[508] AEMAm[509] and APMAm[510–513] have been successfully performed to provide low dispersity polymers with retention of the RAFT end groups. Acetate buffer pH 5 appears to be a suitable polymerization medium.[506,513]

Protonation (with glacial acetic acid solvent) also allows polymerization of other difficult monomers (*e.g.*, 4-vinylimidazole).[514]

Monomers with isocyanate or isothiocyanate groups. Several groups have explored (co)polymerization of monomers containing isocyanate functionality (**119–122**, Table 27).[525–527] 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).[525,526]

Bimodal molecular weight distributions were observed in RAFT polymerization of **120** which was attributed to the presence of trace amounts of water in the polymerization medium.

Monomers with blocked (or protected) isocyanate functionality (**123–125**, Table 28) provide compatibility with a wider range of comonomers and reaction conditions.[528] However, these particular blocked isocyanate are thermally unstable and must be polymerized at low temperature.

The RAFT-synthesis of end-functional polymers and the responsiveness of RAFT-functionality to external stimuli

One of the important features of RAFT polymerization is that the end-groups (R and ZCS_2) of the initial RAFT agent are retained in the product macroRAFT agent. The overall process simply inserts a polymer chain (P_n) between the R and Z–C(=S)S groups of the initial RAFT agent (Schemes 1 and 2). In a well-designed reaction the fraction of chains formed by initiation and termination should be negligibly small. The end group fidelity, which equates to the fraction of living chains (L) can be estimated using the relationships given in the section Initiators in RAFT polymerization above. Thus RAFT polymer-

Table 25 Monomers with active ester or similar functionality used in RAFT (co)polymerization

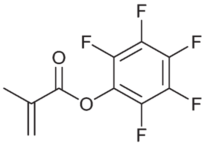
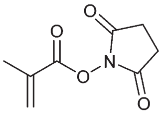
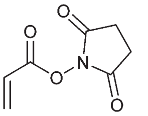
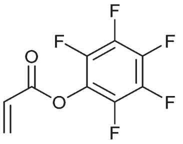
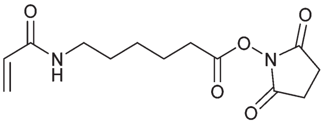
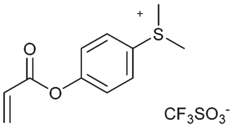
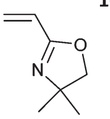
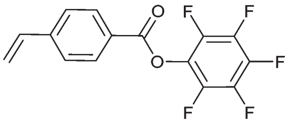
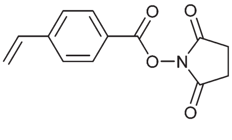
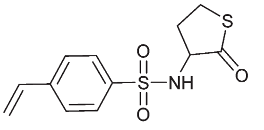
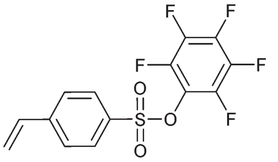
Active ester monomer	Polymerization[a]
 **99** PFPMA	**102**-*co*-LMA (**6**)[478] **102**-*b*-TEGMA (**6**)[479] TEGMA-*b*-**102** (**6**)[479] **102** (**6**)[478,480,481]
 **100** NMS	**100** (**8**)[482] **100**-*co*-PEGMA (**17**)[483] **100**-*co*-HPMA (**2**)[484] **100**-*co*-(vinyl amide)(**38**[b])[485]
 **101** NAS	**101** (**24**)[486] **101** (**30**)[487] **101**-*co*-MMA (**6**)[488] **101**-*co*-DMAm (**9**[c])[489] **101**-*co*-HPMAm (**17**)[89] **101**-*co*-DMAm (**6**[d])[490] **101**-*co*-DMAm (**11**)[491] **101**-*co*-NIPAm (**20**)[492] **101**-*co*-NIPAm (**25**)[493] **101**-*co*-NAM (**14**)[492,494] **101**-*co*-NAM (**11**[e])[495]
 **102** PFPA	**102** (**6**)[480] **102** (**33**)[271] **102** (**13**)[310] **105**-*co*-**102** (**135**)[496]
 **103**	**103**-*co*-MMA (**6**)[488]
 **104**[f]	**104** (**127**)[497] MMA-*b*-**104** (**127**)[498]
 **105**	**105**-*co*-**102** (**135**)[496]
 **106** PFPVB	**106** (**1**)[499]
 **107**	**107**(**128**)[500] **98**-*co*-**107** (**24**)[473]

Table 25 *(Contd.)*

Active ester monomer	Polymerization[a]
 **108**	**108**-*co*-St (**24**)[501]
 **109** PFPVS	**109** (**1**)[499] **109** (**6**)[499] **109** (**13**)[499]

[a] Polymerizations shown as: monomer(s) (RAFT agent)$^{\text{ref}}$. [b] Methyl xanthate used. [c] MacroRAFT formed with **9**. [d] Cholesterol or Pyrene derivative of **6**. [e] Lipid derivative of **11**. [f] The monomer **104** is also a photo-acid generator.

ization is a way of preparing end-functional polymers. The functionality can be present in the R and ZCS_2 or can be formed by transformation of these groups post-RAFT polymerization. In this context we discuss processes for transforming the RAFT end group and the synthesis of polymers with functional RAFT agents. Many of examples relate to the "grafting to" approach for synthesizing functional polymers where a RAFT-synthesized functional polymer is covalently attached to a substrate.

In this section we also consider the chemistry of the thiocarbonylthio RAFT agent functionality, not simply as a RAFT agent, but rather in terms of its responsiveness to pH, light and other stimuli.

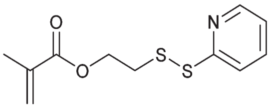
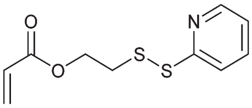
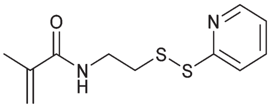
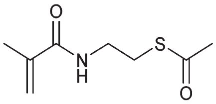
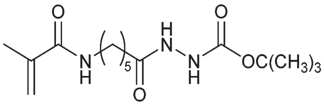
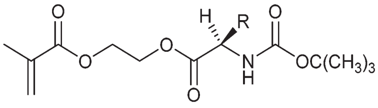
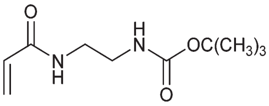
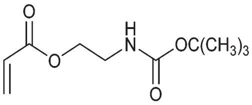
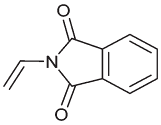
RAFT end-group transformation chemistry

A discussion of RAFT end-group transformation chemistry is of major importance to any consideration of the RAFT-synthesis of stimuli-responsive polymers. End group transformation provides can provide a method of tuning the properties of stimuli-responsive polymers. In other cases, the RAFT end group will need to be removed from the polymers to preclude interference with a desired response. For example, it is known the self-assembly behaviour of hydrophilic or amphiphilic polymers can be influenced by the presence of hydrophobic RAFT agent-derived end-groups,[180,532,533] dithiobenzoate groups quench fluorescence and should be removed to avoid interference with optoelectronic properties.

There are a number of reviews that relate directly to RAFT end group transformation.[534–539] A summary of the procedures available based on our 2011 review[536] is provided in Fig. 6.

The RAFT thiocarbonylthio group can be considered as a protected thiol group. Many of the methods for RAFT end-group transformation involve elaboration of a thiol that can be formed from the thiocarbonylthio group by reduction or through reaction with nucleophiles (Fig. 7).[536,540]

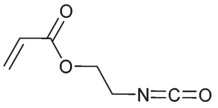
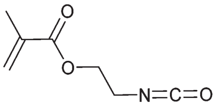
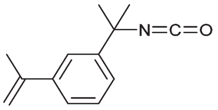
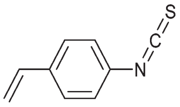
Table 26 Monomers with protected thiol, hydrazide or amino functionality used in RAFT (co)polymerization

Monomer	Ref.
 **110**	515 and 516
 **111**	517
 **112**	518
 **113**	355
 **114**	519
 **115**	304
 **116**	520
 **117**	521
 **118**	98 and 522–524

There are now many examples of forming thiol end groups from RAFT end groups and forming functionality by radical-induced thiol–ene, thiol–yne or thio–Michael reaction either as a separate reaction step or in a one-pot process.[541–549] Other efficient thiol transformation processes include the thiol–epoxy reaction,[550] thiol–halide reaction,[551] thiol–isocyanate reaction,[552] thiol–alkanethiosulfonate reaction[553] and thiol–disufide reaction.[554]

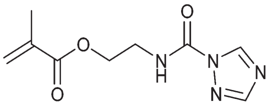
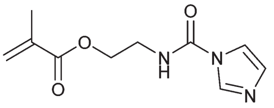
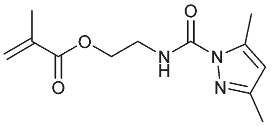
Often processes that provide for complete desulfurization of the polymer are preferred. These include thermolysis,[555–558] radical addition–fragmentation coupling[558,559] and radical addition fragmentation reduction.[180]

Table 27 Monomers with isocyanate or isothiocyanate functionality

Monomer	Polymerization[a]
 **119**	**119** (6)[b] [525] **119** (12)[525] **119** (15)[b] [525] **119** (22)[b] [525]
 **120**	MMA-*b*-(MMA-*co*-**120**) (2)[526]
 **121**	OEGMA-*b*-(**121**-*co*-St) (1)[529] St-*b*-(St-*co*-**121**) (2)[526,530] PEGMA-*b*-(**121**-*co*-MMA) (6)[531] St-*b*-(St-*co*-**121**) (27)[b] [526]
 **122**	**122**-*b*-EA (13)[527]

[a] Polymerizations shown as: monomer(s) (RAFT agent)[ref]. [b] Use of RAFT agents with carboxylic acid functionality provided polymers with bimodal molecular weight distributions.[525,526]

Table 28 Monomers with blocked isocyanate functionality

Monomer	Polymerization[a]
 **123**	**123**(3)[528]
 **124**	**124**(3)[528]
 **125**	**125**(3)[528]

[a] Polymerizations shown as: monomer (RAFT agent)[ref].

A particular challenge, which is of some relevance in the context of this review, is *in situ* end-group removal from polymers in dispersed media. End group oxidation by ozonolysis has been put forward as a possible solution.[560]

Switchable (pH responsive) RAFT agents

As mentioned above, with appropriate selection of 'R', there are RAFT agents that provide control over polymerization of both LAMs and MAMs. However, the level control is less than that required to give very low dispersities and facile polymerization with the full range of monomers.

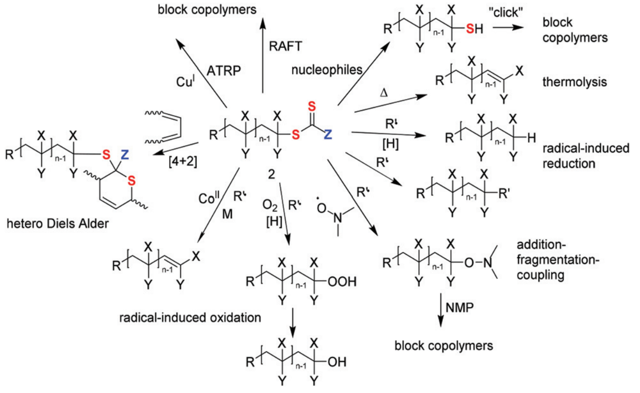


Fig. 6 Processes for RAFT end-group transformation (scheme reproduced with minor changes from ref. 536 © 2011 Society of Chemical Industry). R$'^{\bullet}$ = radical, [H] = hydrogen atom donor, M = monomer.

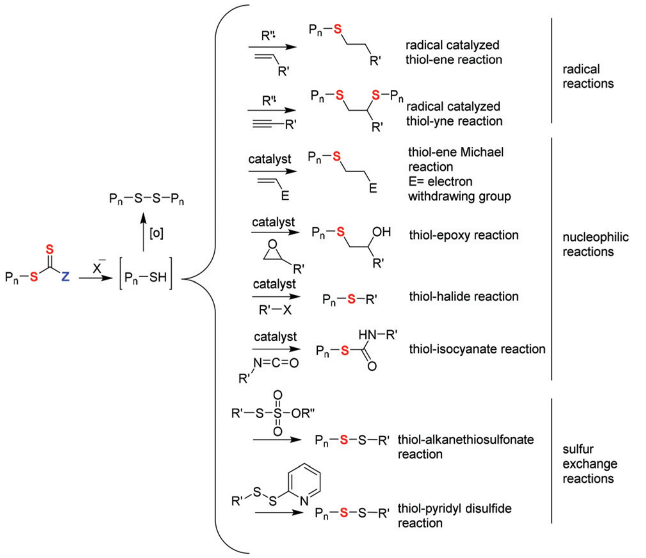


Fig. 7 Reactions of RAFT end-group with nucleophiles with trapping of the thiol end-group formed (scheme reproduced with minor changes from ref. 536 © 2011 Society of Chemical Industry).

Switchable *N*-methyl-*N*-(4-pyridinyl)dithiocarbamate RAFT agents were introduced mainly to provide a viable synthesis of low dispersity polyMAM-*block*-polyLAM.[43,44,122] These RAFT agents can be switched by use of an external stimulus to give very good control over polymerization of both MAMs and LAMs.[44,122] Although a variety of switches may be envisioned most current examples use a pH switch. The RAFT agents are compatible with aqueous media.[51] Developments in this area have now been reviewed.[561] Examples of their application are as follows.

MAMs: St,[43,44,122] MMA,[44,122] MA,[562] BA,[44,122] DMA[51]
LAMs: VAc,[43,44,122,562] NVP[44,122,563]
IAM: NVC[18,44,122,562]

It should be noted that macroRAFT agents formed with LAMs and IAM are extremely acid sensitive and it is important to ensure no acid remains when switching to polymerizae a LAM or IAM.

Initial studies focused on the *N*-methyl-*N*-(4-pyridinyl) dithiocarbamates.[44,122] The *N*-aryl-*N*-(4-pyridinyl) dithiocarbamates are more active with more activated monomers (MAMs) in protonated (switched) form and more active with less activated monomers (LAMS) in non-protonated (unswitched) form.[561,562] Their activity can be tuned through choice of the aryl substituent.[562]

Redox-responsive RAFT agents

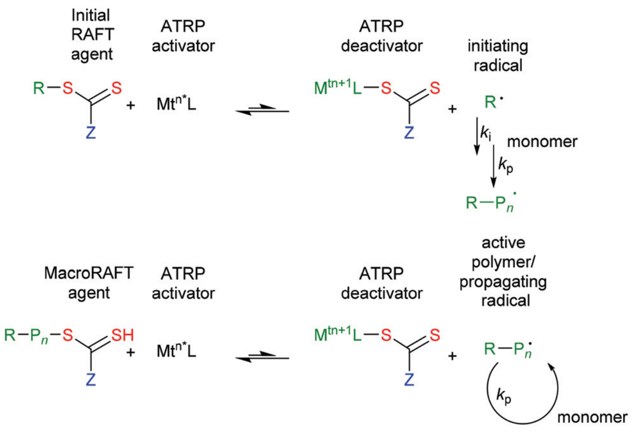
Thiocarbonylthio-compounds have found use as initiators in atom transfer radical polymerization (ATRP). The first reports involved the use of *N*,*N*-dialkyl dithiocarbamate derivatives as ATRP initiators.[564–567] As mentioned above, these reagents do not provide effective RAFT control over the polymerization of more activated monomers (MAMs) so the control mechanism is most likely through an ATRP mechanism with the thiocarbonylthio-compound behaving as a pseudo-halide initiator.

More recently, RAFT agents such as *N*,*N*-diaryldithiocarbamates,[568,569] 1-pyrrolecarbodithioates[570] and dithioesters (1-dithionaphthalates[571,572] and dithiobenzoates[573,574]) have been used in combination with ATRP activators. Under the conditions reported, in that compounds are very effective RAFT agents, the processes should be considered as RAFT polymerizations with ATRA initiation (Scheme 11). Both ISET and OSET mechanisms have been proposed for the ATRA process involving thiocarbonylthio-compounds and Cu(0). It is most likley that all copper mediated ATRA involve a SARA-ATRP (ISET) mechanism.

Light-responsive RAFT agents

There has been recent marked interest in photo-controlled RDRP and, in particular, in polymerizations that can be induced with visible light. Such polymerizations allow for both spatial and temporal control of polymer synthesis.[575,576]

Photo-RAFT may involve may involve RAFT polymerization with a photoinitiator or photo-redox initiator with generation of radicals only from the added initiator.[577] It may involve direct photodissociation of a RAFT agent (without and added photoinitiator or sensitizer). This form of RAFT polymerization should be compared the so-called iniferter method for RDRP described by Otsu and coworkers. As originally described, the process involved polymerization initiated by reversible photodissociation of what we now know to be a poor RAFT agent, usually an *N*,*N*-dialkyldithiocarbamate.[578–580] The method has been reviewed by Otsu and Matsumoto,[581] with respect to the literature through 2000, and more recently by Atilla Tasdelen and Yagci.[582] When instead performed with a good RAFT agent (*e.g.*, a dithiobenzoate or trithiocarbonate)[57,583,584] the dominant mechanism for conveying living characteristics (moleculer weight control) has been shown to be RAFT.[57] Recently, Qiao and coworkers[60,61,585] have shown that very good control in acrylate polymerization can be achieved with visible (blue light) light irradiation. Xu *et al.*[586] (batch) and Gardiner *et al.*[587] (flow) have investigated photo-initiated RAFT of a wider range of monomers under visible light irradiation. Poly *et al.* have exploited xanthate as macroRAFT agents and macro-initiators.[588] Irradiation with lower wavelength light provides for faster polymerization but also more by-products. Irrespective of irradiation wavelength, there is need to pay attention to the rate of radical generation to avoid high radical concentrations and excessive termination.



Scheme 11 Possible ATRA initiation mechanism for RAFT polymerization.

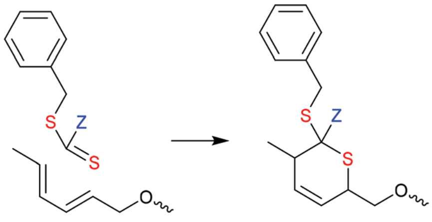
Another important method for photo-RAFT polymerization is PET-RAFT. This may involve (a) photosensitised reversible dissociation of the RAFT agent or (b), a photo-electron transfer process with the RAFT agent or photo-ATRP-like initiation. In all cases, when a good RAFT agent is used, polymerization is most likely controlled by RAFT equilibria. Some monomers/catalysts/RAFT agents for which good control was reported include (see Fig. 2 and Table 25 for monomer abbreviations):

Organometallics
  (MMA, HPMAm)/*fac*-[Ir(ppy)$_3$]/**6**,[65]
  MA/*fac*-[Ir(ppy)$_3$]/(**27** or **33**)[65]
  (OEGA, DMAm, NIPAm, St, Ip)/*fac*-[Ir(ppy)$_3$]/**27**[65]
  MMA/Ru(bpy)$_3$Cl$_2$/**6**[589]
  (MA, St, DMAm)/Ru(bpy)$_3$Cl$_2$/**27**[589]
  (MMA, HPMAm)/ZnTPP/**6**[67]
  (MA, OEGA, DMAEA, DMAm, NIPAm, St)/ZnTPP/**27**[67]
  (MMA, DMAEMA, GMA, HPMAm)/chlorophyll/**6**[590]
  (MA, PFPA, NIPAm)/chlorophyll/**27**[590]
Organic dyes
  MMA/(Fluorescein, Eosin Y or Rhodamine 6G)/**6**[66]
  (HEMA, DMAEMA, MAA, GMA, HPMAm)/(Eosin Y)/**6**[66]
  MMA/pheophorbide/**6**[69]
  NIPAm/curcumin/**33**.[591]

Blocks, multi-blocks, stars and grafts have also been reported.[65,66,69,589] The catalyst choice influences the irradiation wavelength and what RAFT agent or macroRAFT agents can be activated.

Electrocyclic reactions of thiocarbonylthio compounds

Certain RAFT agents undergo reversible electrocyclic reactions with dienes (hetero-Diels Alder reaction) or diazo compounds (1,3-dipolar cycloaddition).



Scheme 12 The thiocarbonyl hetero-Diels Alder process.

Hetero-Diels Alder reaction of thiocarbonylthio compounds. RAFT agents and macroRAFT agents with electron withdrawing ‘Z’ groups have been shown to undergo a hetero-Diels Alder reactions with suitable dienes (Scheme 12).[592–596] The process has been developed as a route to block copolymers,[595,597–601] graft, star and network polymers[594,602,603] and modified surfaces.[592,604,605] The method has precedent in synthetic organic chemistry.[606] Suitable electron-withdrawing ‘Z’ groups include 2-pyridyl, phosphonate or phenylsulfonyl groups. The reaction may be catalyzed by a Bronsted or Lewis acid, *e.g.*, trifluoroacetic acid or zinc chloride, respectively. However, for reaction in aqueous solution no catalyst is necessary.[598] The reaction is thermally reversible[600–602,607] prompting a proposal that it might be used to provide a thermally stimulated colour switch[600,607] or be applied in reversible block copolymer[608] or network formation.[602]

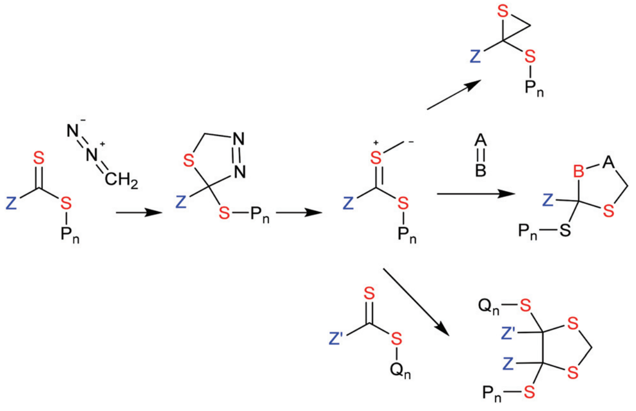
1,3-Dipolar cycloaddition of thiocarbonylthio compounds. Diazomethane undergoes a facile 1,3-dipolar cycloaddition with dithiobenzoate RAFT agents and with dithiobenzoate end-groups of polymers formed by RAFT polymerization.[609] The process does not require a catalyst. For example, 2-cyanoprop-2-yl dithiobenzoate (2), on treatment with diazomethane at ambient temperature (22 °C), provided stereoisomeric 1,3-dithiolanes in near quantitative (>95%) yield.

The process was discovered when attempting to methylate RAFT-synthesized P(MAA) with diazomethane to facilitate characterization.[609] A low molar mass RAFT-synthesized P(MMA) with dithiobenzoate end-groups underwent similar reaction as indicated by immediate decolorization and a quantitative doubling of molar mass. Higher molar mass P(MMA) were also rapidly decolorized by diazomethane and provided a product with a bimodal molar mass distribution.

The process is only seen with more active RAFT agents. The trithiocarbonate group does not react with diazomethane under similar conditions. The proposed mechanism is shown in Scheme 13.

RAFT agents with reactive functionality

RAFT agents containing a variety of reactive functionalities have been designed to enable efficient polymer modification post- or sometimes during RAFT polymerization. These include RAFT agents with active ester functionality (to allow efficient reaction with primary amino groups), with alkyne or azide functionality (to enable modification by Huisgen cycloaddition), with latent amino or thiol functionality or with ene-functionality (usually for use in thiol–ene or ring opening methathesis chemistry). Ideally these functionalities should be inert to the conditions of RAFT polymerization, to reaction with radicals that are likely to be generated and to direct reaction with monomers or with the RAFT thiocarbonylthio group. However this is not always the case for all of the functionalities mentioned.



Scheme 13 Thiocarbonyl 1,3-dipolar cycloaddition reaction. A = B is an unsaturated compound.[609]

RAFT agents with active ester functionality. The major use of RAFT agents containing active ester functionality is in the preparation of other functional RAFT agents rather than mediating RAFT polymerization directly. Nonetheless these RAFT agents can and have been used. Care must be taken in exclude reactive nucleophiles in the polymerization medium. Only examples of dithiobenzoate RAFT agents containing active ester functionality are shown in Table 29. Additional examples are provided in Table S1 (ESI†). The active ester functionalities for the examples shown in Table 29 are substantially more

Table 29 RAFT agents for active ester chemistry

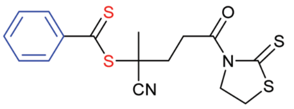
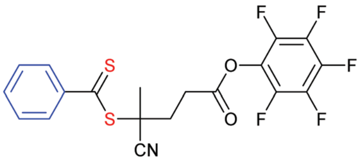
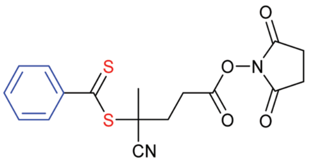
RAFT agent	Monomer(s)
 **126**	Methacrylamides: HPMAm[610] Precursor[490,611–614]
 **127**	Methacrylates: *t*BMA[615] DEGMA[615,616] LMA[616,617] MMA[616] PEGMA[616,617] Methacrylamides: NIPMAm[616]
 **128**	Precursor[191,618–633] Styrenes: **107**[500]

Table 30 Alkyne-functional RAFT agents for Huisgen cycloaddition

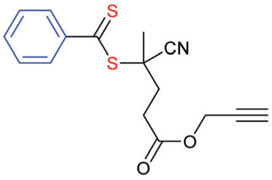
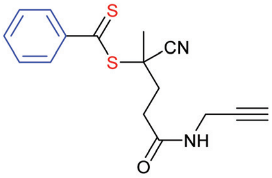
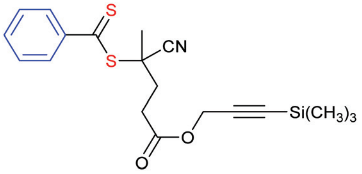
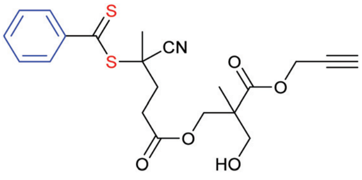
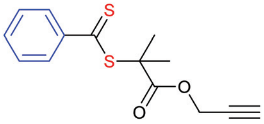
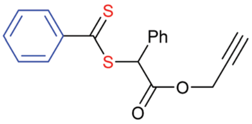
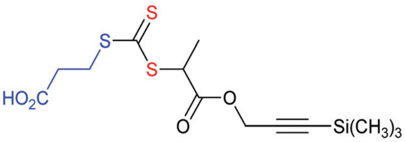
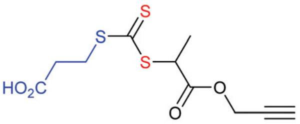
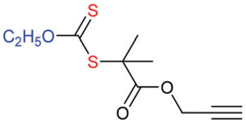
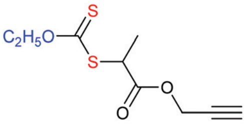
 **129**	Methacrylates: AEMA[634] APMA[635] TESPMA[636] Blocks:[637]
 **130**	Methacrylates: *t*BMA[615] MMA[615] DEGMA[615]
 **131**	Methacrylates:[638] Styrenes: St[639]
 **132**	Acrylates: *t*BA[640]
 **133**	Styrenes: St[101] Blocks: St-*b*-MAH-*b*-NIPAm[101]
 **134**	Blocks: THPA-*b*-St[641]
 **135**	Copolymers: **105**-*co*-**102**[496] Blocks: **105**-*b*-**102**[496]
 **136**	Acrylates: PEGA[642]
 **137**	Precursor:[643] Vinyls: NVP[644]
 **138**	Vinyls: NVP[644]

Table 31 Azide-functional RAFT agents for Huisgen cycloaddition

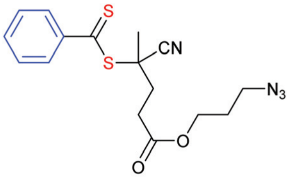
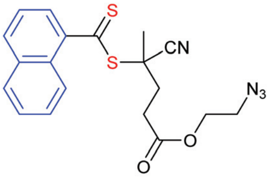
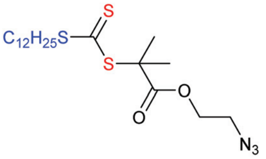
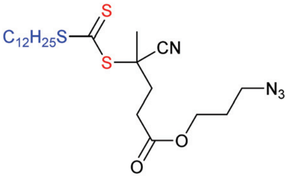
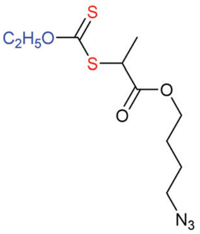
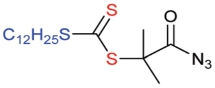
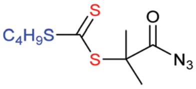
RAFT agent	Monomer(s)
 **139**	Methacrylates: APMA[635] DMAEMA[645,646] MMA[646] Acrylamides: DMAm[647] NIPAm[101] Styrenes: St[101,639,646–648] 2VP[636] 4VP[646] Blocks: DMAM-*b*-St[647] St-*b*-DMAm[647] St-*b*-MAH[101]
 **140**	Styrenes: St[172]
 **141**	Acrylates: BA[169] Acrylamides: DMAm[647] NIPAm[649] Styrenes: S[647] NSS[397] Blocks: St-*b*-DMAm[647] DMAm-*b*-St[647] NIPAm-*b*-DMAm[650]
 **142**	Methacrylates: MAA[651]
 **143**	Vinyls: NVP[652,653]

Table 32 RAFT agents with masked isocyanate functionality

RAFT agent	Monomer(s)
 **144**	Methacrylates: MMA[654] Acrylates: MA[654] Acrylamides: NIPAm[654] Styrenes: St[654,656,657]
 **145**	Methacrylates: MMA[655] Acrylates: BA[655] PEGA[655] Acrylamides: NAM[655] Styrenes: PFS[658]

reactive that the thiocarbonylthio functionality towards, in particular, primary amines. Thus functionalization, conjugation and surface modification pre- or post-RAFT polymerization can be carried out without loss of the RAFT functionality.

RAFT agents for azide–alkyne (Huisgen) cycloaddition. Alkyne and azide functionality for alkyne–azide 1,3-dipolar (Huisgen) cycloaddition can in principle be introduced through the use of appropriate RAFT agents.[596] However, an issue is the reactivity of these groups with radicals, with the monomer(s) or the RAFT agent. RAFT agents containing alkyne functionality are listed in Table 30, those with azide functionality are listed in Table 31. The RAFT agents **129**, **130**, **132–134–136** and **138** with an unprotected alkyne have been successfully used to mediate polymerization of methacrylates. However, while not especially reactive, alkynes are not inert to reaction with radicals.

Azide-functional RAFT agents have been prepared and successfully used in mediating RAFT polymerization. However, there is evidence that azides may react with electron deficient monomers and perhaps thiocarbonylthio RAFT agent functionality under some conditions.

When using RAFT agents with unprotected alkyne or azide functionality it is recommended to use mild reaction conditions and to keep reaction times short.

RAFT agents with isocyanate or masked isocyanate functionality. The carbonyl azide functionality of **144** and **145** undergoes a Curtius rearrangement to form isocyanate functionality during RAFT polymerization at 60 °C (Table 32). The process has been used to form polymers with isocyanate ends and for RAFT polymerization with concurrent isocyanate formation and reaction.[654,655] A low molecular weight amine (benzylamine) or an alcohol (propargyl alcohol) were used as reaction partners for the isocyanate ends. Remarkably, no aminolysis of the RAFT thiocarbonylthio group was observed with benzylamine for the polymerization conditions used.

Table 33 RAFT agents with ene functionality

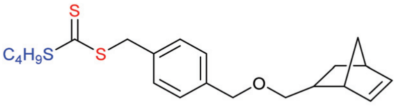
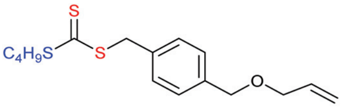
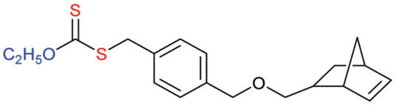
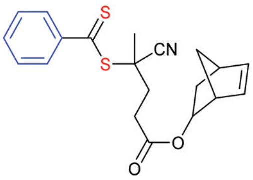
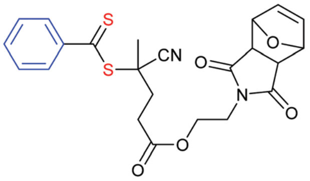
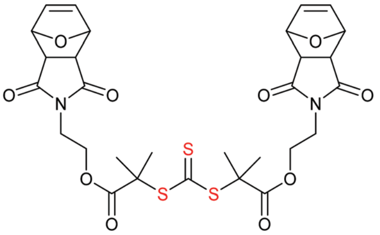
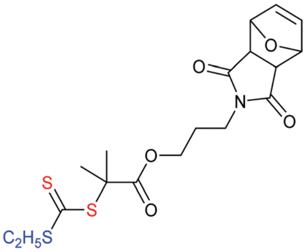
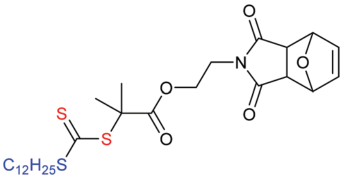
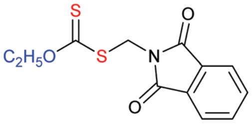
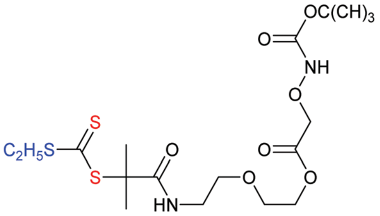
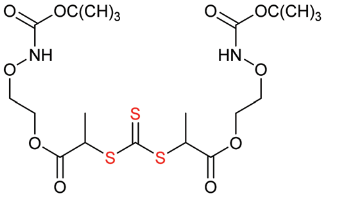
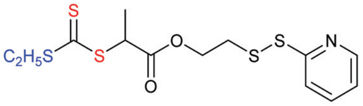
RAFT agent	Monomer(s)
 **146**	Acrylates: EEA, MA[666] Styrenes: St[654,656,657,666]
 **147**	Styrenes: St[654,656,657,666]
 **148**	Vinyls: VAc[666]
	Methacrylates: MMA[667] Acrylates: MA[667] Styrenes: St[667]
 **149**	Methacrylates: MMA[659] OEGMA[660]
	Methacrylates: MMA[659]
	Acrylates: HPA[661] OEGA[661]
	Styrenes: St[662,665] Acrylamides: NIPAm[662,663]

Table 34 RAFT agents with latent primary amino-functionality

RAFT agent	Monomer(s)
31 	Acrylates: BA[668,669] Styrenes: St[669,670] Acrylamides: NIPAm[668,669,671] DEAm[672] DMAm[671] Vinyls: VAc,[668,673,674] NVP[668,675] NVP copolymer[676]
	Acrylamides: NIPAm[677]
	Acrylates: PEGA[678]
 **150**	Styrenes: 60[334]

RAFT agents with ene or diene functionality. RAFT agents with norbornene functionality have been prepared and successfully used in RAFT polymerization of methacrylates (MMA) and styrene to form low dispersity polymers (Table 33). Broader dispersities for longer reaction times were seen with MA which was attributed to reactivity of the norbornene in copolymerization. The norbornene functionality can be subsequently used in thiol–ene or ring-opening metathesis processes.

Ene-functionality that is reactive in radical polymerization must be protected. For example maleimide functionality is usually used in the form of a Diels–Alder adduct. When again deprotected, maleimide end-functional polymers are used in forming conjugates by thio–Michael reaction,[659–661] or Diels Alder or other electrocyclic reaction.[662,663] Maleimide-based structures have a long-established history in bioconjugate chemistry.[664] The protected maleimide chain-end is an ene-functional polymer in its own right and a potential macromonomer in ring-opening metathesis polymerization.[665]

RAFT agents with latent primary amino or thiol-functionality. While it possible to carry out reaction between substrates containing RAFT agent functionality (*e.g.*, those also comprising active esters) and primary amines, in general, the thiocarbonylthio group and the primary amine are incompatible, and the primary amine functionality must generally be protected in some way. Common forms of protected amines are the phthalimido-group and the *t*BOC-group both of which have been used in RAFT agents (Table 34).

Similar considerations apply in the case of other nucleophilic groups. Free thiol functionality also needs to be protected.

Conclusions

RAFT is an extremely versatile process for forming stimuli-responsive polymers. The stimuli-responsive elements of RAFT-synthesized polymers may originate from functionality present in the RAFT agent or macroRAFT agent, the monomers polymerized, or might be incorporated post-polymerization by transformation of a RAFT-synthesized polymer. Many functionalities can be introduced directly with the use of appropriately designed monomers or RAFT agents. In the rare case where this is not possible, there exist many possibilities for modification of RAFT-synthesized polymers post-polymerization.

The aim of this paper has been to illustrate how RAFT process can be applied in this context, by pointing out the features necessary to achieve the desired level of control and providing key references to the now vast literature on this application.

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