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ScienceDirect

Polymer 48 (2007) 6467−6480

polymer

www.elsevier.com/locate/polymer

Feature Article

The application of ionizing radiation in reversible addition−fragmentation chain transfer (RAFT) polymerization: Renaissance of a key synthetic and kinetic tool

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Received 18 June 2007; received in revised form 31 July 2007; accepted 15 August 2007
Available online 22 August 2007

Abstract

Ionizing radiation, such as γ, ultraviolet, microwave and X-ray radiation, has long been used in polymer chemistry as a means of initiating polymerization, crosslinking gels and decomposing particular polymer components. More recently, ionizing radiation has found application in tandem with living radical polymerization to form novel polymeric materials with defined molecular weight and narrow molecular weight distribution. In particular, γ-rays and ultraviolet light both have shown promise as sources of initiation in reversible addition−fragmentation chain transfer (RAFT) polymerization. The ability to apply these sources of initiation at low temperatures is useful in applications where elevated temperature is likely to be detrimental to the system, for instance, in preparing protein−polymer conjugates. Similarly, the use of these initiating sources at low temperature is particularly suitable for some monomers, such as allyl compounds, which have not been synthesized using any other living radical approach. The current review examines the development of ionizing radiation as a tool in RAFT polymerization, with particular reference to the elucidation of the polymerization mechanism, the synthesis of high functionality polymers and probing the kinetic parameters of the RAFT process.

Keywords: Living/controlled radical polymerization; Radiation; Synthesis

1. Introduction

Living polymers are those in which the polymer chains have a functional end which can be used as an initiating site for subsequent additional polymerization [1]. The development of living polymerization methodologies has led to a generational leap in the complexity of polymer materials which are able to be synthesized, including block [2], star [3], comb [4] and gradient [5] copolymers. However, the initial techniques used for living polymerization (anionic [6] and cationic [7] polymerization) tended to be applicable to only a limited array of monomers, and are − in the case of anionic polymerization − extremely sensitive to impurities such as water. These limitations drove the development of more versatile, free radical processes which were also ‘‘living’’ in nature. To this end, reversible termination polymerization (including nitroxide [8] and thioiniferter [9] mediated systems), atom transfer radical polymerization [10,11] and reversible addition−fragmentation chain transfer (RAFT) polymerization [12] have all been explored as methodologies for performing living radical polymerization. Of these approaches, RAFT has shown particular promise because of the relative insensitivity of the chemistry to functional groups in the monomers polymerized, i.e. in cases where protecting group chemistry would previously have been required, the RAFT approach can be used directly on the desired monomer. This has generated considerable research interest in the technique since its introduction almost 10 years ago [13−20].

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doi:10.1016/j.polymer.2007.08.043

The most common example of RAFT polymerization involves free radical polymerization in the presence of thiocarbonylthio compounds, such as dithioesters, trithiocarbonates, dithiocarbamates and xanthates. In these cases, the polymerization proceeds (in its simplest form) via the mechanism depicted in Fig. 1. Initially, radicals are generated via either thermal self-initiation of the monomer or via thermal decomposition of an added initiator (Fig. 1, step (i)). These radicals subsequently initiate polymerization, as would be expected in a conventional free radical polymerization reaction (step (ii)). However, rather than simply propagating and then terminating, the radical chains are also able to undergo addition to the electron rich thiocarbonyl group in the thiocarbonylthio compound (step (iii)). This results in the formation of an intermediate radical adduct, the fate of which has been the subject of considerable debate in the literature [21–26]. Fragmentation of the adduct is possible in either direction, though it is important for this to favor the expulsion of the R group in the first instance in order to ensure that the bulk of the chains is initiated at the same time (through step (vi)). The efficient expulsion is vital for the evolution of molecular weights to be incremental with conversion. The polymer formed through this process then possesses a chain transfer moiety as an end group, allowing the polymer to act as a macromolecular chain transfer agent by the same mechanism as outlined above. A dynamic equilibrium is thereby established, in which propagating chains undergo continuous chain transfer events as the polymerization proceeds (step (v)), ensuring that termination is minimized and that the resulting polymerization is ‘‘living’’. Of course, some termination events will continue to take place via the typical termination processes in free radical polymerization. While evidence for the termination of the intermediate radicals formed in steps (iii) and (v) is scant, such reactions can nevertheless not be ruled out.

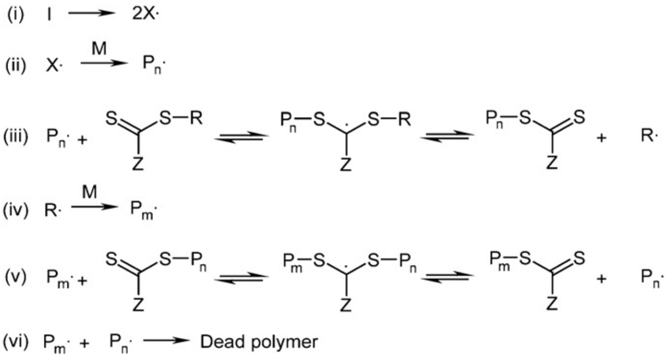
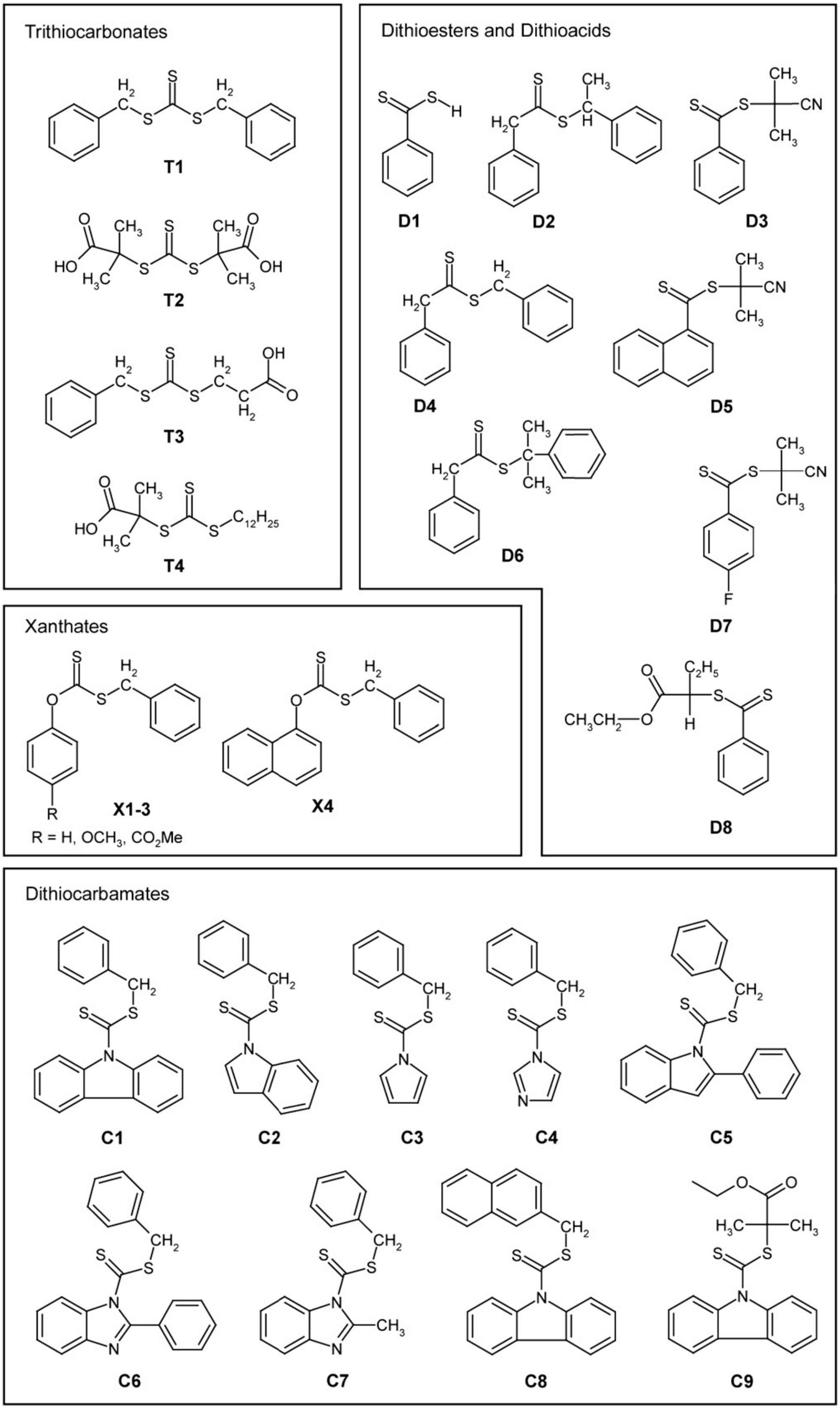


Fig. 1. The mechanism of reversible addition–fragmentation chain transfer (RAFT) polymerization. (i) Radicals are formed through the decomposition of an added thermal- or photoinitiator or by exposure of the polymerization solution to ionizing radiation. Ionizing radiation may result in the formation of monomer, solvent or RAFT agent-derived radical species. (ii) The radicals formed initiate polymerization. (iii) The propagating radicals undergo chain transfer with thiocarbonylthio compounds, resulting in polymer chains bearing thiocarbonylthio chain transfer moieties. (iv) ‘‘R’’ groups liberated from the initial chain transfer event then initiate further chains. (v) Polymerization proceeds with continuous chain transfer events occurring with the thiocarbonylthio terminated chains, leading to a reduction of other termination and transfer events. (vi) Nevertheless, some chains are lost through conventional termination.

For many decades, ionizing radiation has been a useful tool in synthetic polymer chemistry, for applications such as crosslinking [27], selective decomposition of secondary components [28], and initiating radical polymerization reactions [29]. The last six years have seen an increasing level of interest in the convergence of ionizing radiation-initiated polymerization with RAFT polymerization, to the extent where a significant array of polymers has now been prepared using this approach [30–69]. The use of ionizing radiation in tandem with RAFT offers a number of advantages over conventional initiation mechanisms. Most notably, the approach can be applied at ambient temperature, abrogating the need to generate radicals via thermal decomposition of an azo- or peroxy-initiator. Further, initiation via ionizing radiation can be applied for indefinite time periods, well after a traditional thermal initiator would have been exhausted. From a kinetic standpoint, the radical flux which is generated by a radiation source varies much less dramatically with temperature than the radical flux generated by a thermally labile compound, and is therefore useful in kinetic and mechanistic investigations. Moreover, initiation can be switched off instantaneously, simply by removal of the initiation source. Ionizing radiation has already been used in the preparation of a wide array of well defined polymers using a number of different chain transfer agents (see Fig. 2). Importantly, some of these polymers have not been synthesized in a living manner using any other initiation approach. Herein, we will summarize the initial work in this burgeoning area, with regard to both the polymers synthesized and the mechanism of polymerization. Particular emphasis will be given to examples where the final polymers are likely to find applications that may not necessarily be available by following other synthetic approaches. The areas to be examined in detail are (i) γ-initiated polymerization, (ii) UV-initiated polymerization and (iii) plasma initiated polymerization.

2. γ-Initiated RAFT polymerization: genesis and mechanistic elucidation

The first report on living radical polymerization in the presence of thiocarbonylthio compounds was reported by Pan and co-workers in 2001 [30]. In this case, polymerization of methyl acrylate (MA), styrene (Sty) and methyl methacrylate (MMA) was performed in the presence of dibenzyl trithiocabonate (Fig. 2, **T1**). The PMA molecules synthesized were typically of narrow molecular weight distribution (polydispersity index (PDI) < 1.2), with the theoretical molecular weight agreeing well with that predicted from stoichiometric calculation (Fig. 3). The PSty and PMMA synthesized also showed good agreement between theoretical and experimental molecular weight, although in these cases the molecular weight distributions were somewhat broader than those for PMA (PDI 1.2–1.4). The authors proposed a mechanism for the polymerization whereby the γ radiation induced sequential homolytic cleavage of the *S*-benzyl linkage in **T1**, thereby liberating an initiating species (the benzyl radical) and a thiocarbonylthiyl radical which is ‘‘dormant’’ and therefore reversibly


Trithiocarbonates

T1

T2

T3

T4

Dithioesters and Dithioacids

D1 D2 D3

D4 D5

D6 D7

D8

Xanthates

X1-3

X4

R = H, OCH_3, CO_2Me

Dithiocarbamates

C1 C2 C3 C4 C5

C6 C7 C8 C9

Fig. 2. Thiocarbonylthio compounds used in RAFT polymerization under ionizing radiation. (Adapted from Refs. [11–48].)

terminates the growing polymer chains. This is a similar mechanism to that proposed by Otsu for living photopolymerization in the presence of dithiocarbamates [70]. The evidence proposed for this mechanism was the structure of the final polymer chains, which were shown to have benzyl moieties at either end of the chain and the trithiocarbonate

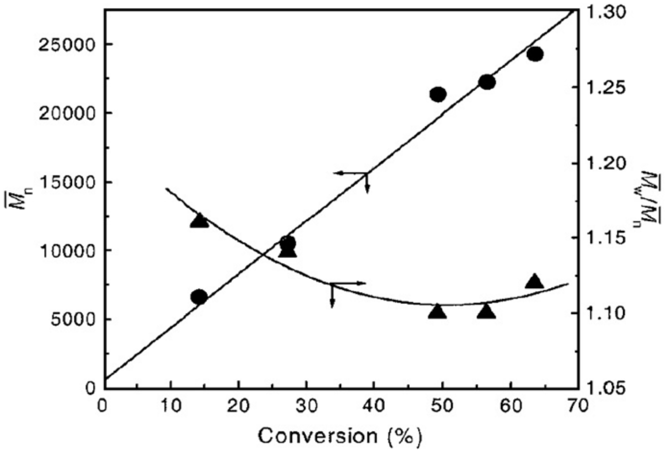


Fig. 3. The evolution of molecular weight and polydispersity index with increasing conversion for dibenzyl trithiocarbonate (**T1**) mediated bulk polymerization of methyl acrylate. The γ-radiation dose rate was 80 Gy min^{-1}, and [**T1**] = 0.6 wt%. (Reproduced with kind permission from Ref. [30].)

moiety in the centre. This was shown using NMR studies to prove that the sulfur atoms were adjacent to the head group of the monomers used, while the benzyl group had clearly added to the tail of the monomer. Such a structure, while consistent with the reversible termination mechanism proposed, would also be expected for polymer formed through a RAFT process. This will be discussed in further detail below.

Following the initial report, Pan and co-workers demonstrated the efficacy of using living radical polymerization under a constant source of γ radiation for preparing block copolymers with PSty and PMA domains [31]. This was achieved by again using **T1** as the added thiocarbonylthio compound, and polymerizing an initial precursor polymer of PSty. This was then chain extended with MA to give PSty–PMA–PSty (the symmetrical nature of **T1** ensures that the initial block ultimately ''brackets'' the final polymer added). The authors were able to form the polymers using both PSty and PMA as the initial block, though in the case where PMA was used initially the final polymers tended to have a substantially broader molecular weight distribution than when PSty was used as the starting point (PDI = 1.37 versus 1.18, for an equivalent total molecular weight). These results were important in that they demonstrated that the approach was useful not only in the preparation of homopolymers, but also in the synthesis of more sophisticated molecular architectures.

Almost simultaneously to the investigations of block copolymer synthesis, Pan and co-workers also published on the use of dithiobenzoic acid (Fig. 2, **D1**) as an agent for mediating polymerization under γ radiation [32]. In this case, the authors observed that polymerization of both MA and Sty could be effectively controlled using this agent, and that the evolution of molecular weight with conversion in these two cases was shown to correlate very closely with that predicted from theory. Importantly, the molecular weight determined from GPC was verified with that from NMR, and the two values were shown to agree very closely. However, one limitation of using **D1** as an additive for controlling the molecular weight of PSty and PMA is that the polymers formed tended to have a slightly broader molecular weight distribution than did those prepared using **T1** (1.4 compared with 1.1–1.3). Nevertheless, the application of this agent did demonstrate that the observed living behaviour was not unique to **T1**, but could also be achieved using other thiocarbonylthio agents.

Independent investigations by the Centre for Advanced Macromolecular Design (CAMD) group around the same time were exploring the use of γ radiation to initiate the polymerization of styrene in the presence of the RAFT agent 1-phenylethyl phenyldithioacetate (Fig. 2, **D2**) [33]. In these studies, the authors observed excellent agreement between the theoretical and the experimental molecular weights, and that the molecular weight distributions were quite narrow (PDI < 1.2). The effect of the radiation dose rate on the polymerization was also investigated, and it was determined that the rate of polymerization increased with the square root of the dose rate. As such, higher conversion polymers could be obtained for a given time period by increasing the dose rate, with little obvious effect on the molecular weight distribution. Unlike the earlier studies by Pan and co-workers, these studies explained the observed living behaviour by invoking a RAFT mechanism for the polymerization. Importantly, none of these early studies provided irrefutable evidence of the mechanism which was operative during the polymerization. In order to elucidate the polymerization mechanism, further studies would be required.

To this end, Rizzardo and co-workers performed the polymerization of methyl methacrylate in the presence of two different thiocarbonylthio species [34]. These two agents were specifically selected due to the nature of the ''R'' moiety. In one case, the R group was 2-cyanoprop-2-yl, an excellent leaving group with respect to methacrylyl which would be expected to lead to living radical polymerization under a RAFT mechanism (see Fig. 2, **D3**, for the specific agent used). In the other case, the R group chosen was 1-phenylethyl, a poor leaving group with respect to methacrylyl, which would therefore be expected to give non-living behaviour if a RAFT system was operative: fragmentation would be overwhelmingly in the direction of the methacrylyl radicals, leading to the absence of an R-initiated, incrementally propagating population. In contrast, under the reversible termination mechanism proposed by Pan and co-workers, *both* agents should give living behaviour because both 2-cyanoprop-2-yl and 1-phenylethyl radicals are capable of initiating MMA polymerization. Polymerization experiments demonstrated that living behaviour was only evident when the leaving group was appropriate for the propagating polymer chains, that is, when 2-cyanoprop-2-yl was the leaving group (see Fig. 4). This provided the first clear evidence that the mechanism of living polymerization under γ radiation was proceeding via a RAFT mechanism. Such an observation was perhaps not unexpected, as the initial agent used by Pan and co-workers, **T1**, had been previously used in a thermally initiated RAFT polymerization [14]. It is unlikely that radical addition to the thiocarbonyl, and subsequent fragmentation events, could be prevented simply because the origin of the radicals was different.

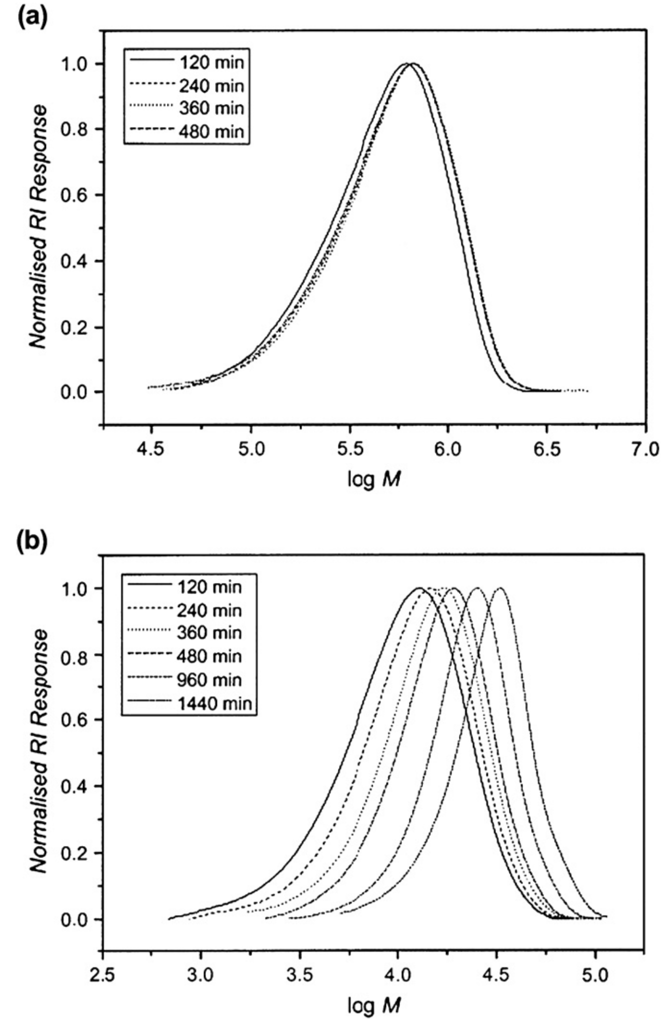


Fig. 4. Evolution of molecular weight distribution with time for MMA polymerization at 23 °C in the presence of (a) 1-phenylethyl dithiobenzoate, [PEDB] = 8.2 mmol L^{-1} and (b) 2-cyanoprop-2-yl dithiobenzoate (**D4**) [**D4**] = 8.1 mmol L^{-1}. The γ-radiation dose rate was 0.18 kGy h^{-1}. (Reproduced with kind permission from Ref. [34].)

Importantly, there was one example reported by Pan and co-workers which could not be explained using the RAFT mechanism, that being the polymerization of MMA in the presence of **T1** [30]. When using **T1** to mediate the polymerization, the leaving groups are necessarily benzyl, and are, as such, poor leaving groups with respect to methacrylyl groups. Pan and co-workers nevertheless did observe living behaviour using this combination of compounds, whereas Rizzardo and co-workers were unable to achieve the same result – instead, broad molecular weight distributions which did not change with conversion were observed [34]. The origin of this discrepancy may lie in the vastly different dose rates used: 4.8 kGy h^{-1} by Pan and co-workers compared with 0.18 kGy h^{-1} by Rizzardo and co-workers. Further investigation is required to reconcile these two conflicting reports.

Since the initial reports of γ-initiated living polymerization in the presence of thiocarbonylthio compounds and the subsequent exploration of the polymerization mechanism, there has been considerable effort expended in polymerizing a number of different monomers in the presence of a variety of thiocarbonylthio compounds. To date, trithiocarbonates [30,31], xanthates [35], dithiocarbamates [36–38] and dithioesters [33,34,39] have all been used as chain transfer agents in the polymerization. Pan and co-workers successfully applied a number of xanthates (**X1**–**X4**) in the polymerization of methyl acrylate (MA) under γ radiation [35]. In these experiments, it was demonstrated that the presence of a *para*-substituent on the phenyl had little bearing on the rate of polymerization, while replacing the phenyl moiety with a naphthyl group led to a marked decrease in the rate of polymerization. In all cases, γ initiated, xanthate mediated polymerization of MA yielded polymers with narrow molecular weight distribution (PDI < 1.2), and molecular weight which agreed well with the theoretical value. Additionally, the authors also demonstrated that styrene could be polymerized in the presence of **X1** to give a living polymer, although in this case the polymerization was severely retarded and the molecular weight distribution of the polymers formed was not especially narrow (PDI = 1.4–1.5). Living polymerization of methyl methacrylate (MMA) in the presence of **X1** was attempted, though in this case no living behaviour was observed. This observation is likely due to the thiocarbonyl group in **X1** not being active to addition of methacrylyl radicals, along with the unsuitability of the benzyl leaving group with respect to the propagating radicals.

Polymerization under γ radiation in the presence of dithiocarbamates has been explored by a number of groups [36–38]. Both Pan and co-workers [36,37] and Zhu and co-workers [38] have demonstrated the efficacy of aromatic dithiocarbamates for mediating the polymerization of MA under γ radiation. The initial studies used a number of aromatic dithiocarbamates with benzyl leaving groups (Fig. 2, **C1**–**C4**) as chain transfer agents, and resulted in polymers with excellent living characteristics [36,37]. Importantly, these authors also demonstrated that using a non-aromatic dithiocarbamate (1-benzyl-*N*,*N*-diethyl dithiocarbamate) resulted in complete failure to control the polymerization: the resulting polymers were either of very broad molecular weight distribution and high molecular weight, or, at higher total doses, completely crosslinked. Zhu et al. also explored the polymerization of methyl acrylate in the presence of a selection of dithiocarbamates (Fig. 2, **C5**–**C9**) [38]. In each of these cases, the polymers formed were of relatively narrow molecular weight distribution, and the molecular weight showed good agreement with that calculated stoichiometrically. Importantly, these authors reached the same conclusion as Pan and co-workers regarding the polymerization under γ radiation in the presence of *N*,*N*-dialkyl dithiocarbamates. Further, the authors observed a dependence in the rate of polymerization on the structure of the heteroatom ring, with polymerization in the presence of **C5** being more strongly retarded than that in the presence of **C6**. The authors attributed this difference in the rate of polymerization to the relative stabilities of the intermediate radicals formed during the polymerization.

One of the more commonly studied families of thiocarbonylthio compounds in classical RAFT polymerization has been the dithioesters, and researchers investigating living radical polymerization under γ radiation have used these compounds extensively to mediate the polymerization [33,34,39–41]. However, one important limitation which should be borne in mind with this approach is that some types of dithioester, such as dithiobenzoates [34] and dithionaphthalates [41], often induce very strong retardation of polymerization reactions. Furthermore, this phenomenon is exacerbated at low temperatures [71]. For this reason, the bulk of research into γ-initiated RAFT polymerization has utilized non-dithiobenzoates, such as phenyldithioacetates (e.g., Fig. 2, **D2**, **D4** and **D6**) [34]. The most notable exception to this rule is the polymerization of MMA in the presence of either 2-cyanoprop-2-yl dithiobenzoate (**D3**) or 2-cyanoprop-2-yl dithionaphthalate (**D5**) [41]. In these cases, the polymerization likely proceeds because of the superior leaving group ability of methacrylyl groups, as opposed to acrylyl or styryl groups which will form a more stable adduct. Attempts to polymerize other monomers (such as MA) at room temperature in the presence of dithiobenzoates under γ radiation have thus far proven unsuccessful, with the polymerization effectively completely inhibited. These results demonstrate that the temperature of polymerization must also be considered when designing an appropriate monomer–CTA system for use under γ radiation.

Recent explorations by Barner-Kowollik and co-workers have probed the nature of the initiating species in the γ-initiated polymerization of both MA and BA in the presence of 2-phenylprop-2-yl phenyldithioacetate (**D6**), a commonly used dithioester [42]. By examining the high resolution electrospray ionization mass spectra (ESI-MS) of the polymer products, it can be demonstrated that the principle distributions of polymers are those that are terminated by the expected R and Z groups. However, a small yet significant population of chains initiated by phenyldithioacetate fragments is also evident, along with chains initiated through the products of water radiolysis and γ derived fragments of the monomer species. Furthermore, it is evident that there is some conversion of the dithioester end groups into thiol groups, and subsequent coupling of these thiols to form disulfide linkages. The data are extremely valuable in that it shows the complexity of the initiation pathways which are operating in γ-initiated RAFT polymerization. In a subsequent study, Barner-Kowollik and co-workers mapped the end groups – also via high resolution ESI-MS using quadrupole and quadrupole time of flight detectors (Q-TOF) – formed in γ-initiated *N*-isopropylacrylamide (NIPAAm) and acrylic acid (AA) polymerizations [43]. Such "smart" polymers and their associated polymer–protein conjugates find a vast array of biomedical applications. Ambient temperature RAFT polymerizations conducted in an aqueous environment are a favorable method of choice for the synthesis of these materials; however, information regarding the initiation mechanisms behind these polymerizations – and thus the critical polymer end groups – is lacking. It was found that trithiocarbonate and $^{\bullet}$R radicals produced from the radiolysis of RAFT agent; $^{\bullet}$OH and $^{\bullet}$OOH radicals produced from the radiolysis of water; and $^{\bullet}$H radicals produced from the radiolysis of water, RAFT agent or monomer are capable of initiating polymerizations, and thus contribute towards the generated chain ends. A typical high resolution mass spectrum alongside the derived end group in AA and NIPAAm γ-initiated RAFT polymerization in aqueous media is given in Fig. 5. Additionally, thiol terminated chains are formed via the degradation of trithiocarbonate end groups. This study is the first to provide a comprehensive mapping of the formation pathways and end group patterns of stimuli-responsive polymers, thus allowing the design and implementation of these materials to proceed in a more tailored fashion.

Interestingly, in a number of the examples discussed above, the polymerization of the neat monomer in the absence of a thiocarbonylthio compound leads not only to polymer with broad molecular weight distribution and uncontrolled molecular weight, but also to polymers which are completely crosslinked. It is possible that these crosslinking reactions are reduced by the presence of the thiocarbonyl groups, which reduce the extent to which radical reactions occur by acting as effective radical sinks. This demonstrates the efficacy of combining RAFT chemistry with γ radiation to exert substantially greater control than has historically been possible over γ-initiated polymerization.

While there are a number of reports, as discussed above, on the use of this chemistry to polymerize common monomers, one of the key benefits of using RAFT is that it affords the ability to produce higher order molecular architectures. In the following section we examine the work completed, to date, on using γ radiation and RAFT to prepare such molecular structures.

3. γ-Initiated RAFT polymerization: evolving to advanced molecular architectures

The use of cyclic thiocarbonylthio compounds allows the possibility of preparing ring shaped macromolecular structures, which are likely to have substantially different properties to the analogous linear polymers. Pan and co-workers [44] and Bai and co-workers [45] have each studied examples in which γ radiation was used alongside the addition of a cyclic thiocarbonylthio compound to polymerize MA to form a cyclic macromolecular product. Bai et al. employed the use of a cyclic trithiocarbonate [45], while Pan's group used a cyclic dithiobenzoate [44]. In both cases, the polymerization is conducted at extremely low temperatures (in Bai's study at −76 °C and in Pan's study at −30 °C), and the authors propose a ring opening and monomer insertion mechanism. The rationale for using low temperature was to reduce the diffusion rate and therefore the number of side reactions occurring, ensuring that the principle product formed was cyclic, rather than linear, polymer. This is reflected in Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) measurements, where an increasing proportion of linear polymer was observed with increasing temperature. Additionally, in the study by Pan and co-workers [44], the addition of *N*-isopropylacrylamide (NiPAAm) to the cyclic PMA in the presence of γ radiation led to the formation of PNiPAAm–PMA–PNiPAAm cyclic polymers. These

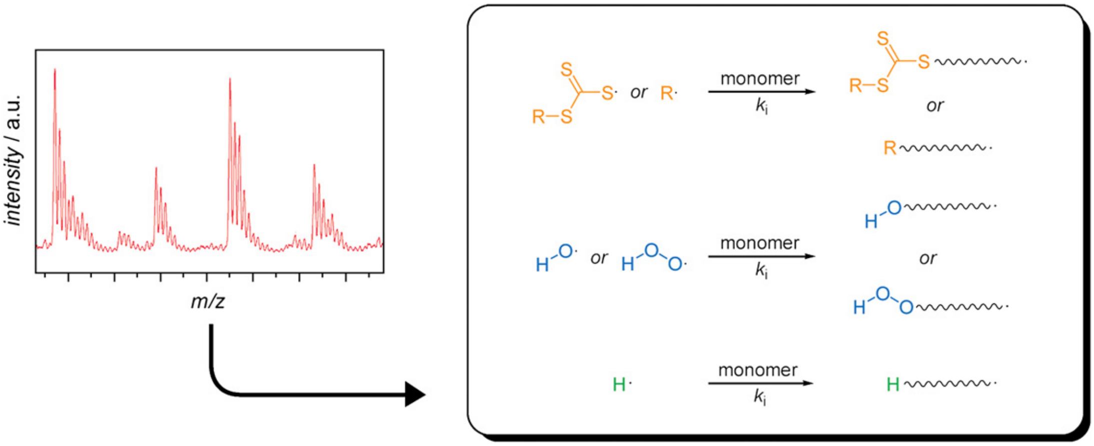


Fig. 5. End groups derived from electrospray ionization mass spectrometry of PNiPAAm and PAA generated during trithiocarbonate (*S*,*S*-bis(α,α′-dimethyl-α″-acetic acid)trithiocarbonate) mediated polymerization and γ-initiated polymerization in aqueous medium at ambient temperature.

results demonstrate that, by appropriate selection of the starting materials and reaction conditions, γ radiation can be used to initiate the polymerization of extremely sophisticated materials.

The polymerization of block copolymers is an area of considerable international interest. While the earlier studies of γ-initiated RAFT polymerization examined the formation of blocks from common monomers as proof-of-principle, the formation of blocks from more complex functional monomers is also highly desirable. To this end, Millard et al. have examined the formation of block copolymers incorporating the pH responsive moiety poly(acrylic acid) (PAA) and the temperature responsive moiety PNiPAAm [46]. These are particularly interesting as the solubility of the final block copolymer formed is dependent on both the pH and the temperature of the solution. γ-Initiated living radical polymerization of these polymers was successfully performed in aqueous solution in the presence of two different RAFT agents: *S*,*S*-bis-α,α′-dimethyl-α″-acetic acid trithiocarbonate (Fig. 2, **T2**) and 3-benzylsulfanylthiocarbonylsulfanyl propionic acid (Fig. 2, **T3**). Homopolymers of PNiPAAm and PAA could be prepared using either chain transfer agent, while block copolymers were formed by polymerizing either monomer in the presence of **T2**, and then chain extending with the other monomer. In all cases, the molecular weight distributions remained narrow, with PDI < 1.2.

Pan and co-workers have also formed block copolymers incorporating temperature sensitive PNiPAAm domains [47]. In this case, γ radiation was used to initiate the polymerization of poly(ethylene oxide monomethyl ether) methacrylate (MPEO-MA) in the presence of **T1**. This is in itself an interesting result, as methacrylate monomers cannot usually be polymerized in a living manner in the presence of benzyl leaving group RAFT agents. The resulting polymers (which had a PDI < 1.3) were then further polymerized with NiPAAm (see Fig. 6). The final polymer had an even narrower molecular weight distribution (PDI < 1.2), and showed lower critical solution temperature behaviour typical of homo- and copolymers of PNiPAAm, with an LCST of 33.5 °C. Taken together with the previous study of Millard et al. [46], these results suggest that γ-initiated RAFT polymerization is an effective means of polymerizing a number of water-soluble soluble block copolymers, without compromising the polymers' stimuli-responsive properties.

The preparation of amphiphilic copolymers using γ-initiated RAFT has been the subject of recent investigations by Zhang and co-workers [48]. In this case, poly(*tert*-butyl methacrylate) (P*t*BMA) and poly(*n*-butyl methacrylate) (P*n*BMA) were combined together in a sealed tube with 2-phenylprop-2yl dithiobenzoate (**D3**), and subsequently polymerized under a constant source of γ radiation. Amphiphilic copolymers were prepared via hydrolysis of the *tert*-butyl groups to yield methacrylic acid groups. By varying the proportion of the *tert*-butyl functionalized monomer, the authors were able to prepare final polymers with varying proportions of methacrylic acid groups. The authors demonstrated that the narrow molecular weight distribution polymers prepared were able to be used as polymeric surfactants in the preparation of polystyrene emulsions, with the size distribution of the particles directly affected by the composition of the polymeric surfactant used.

The same group have also examined the preparation of novel gradient polymers using terpolymerization of *N*-vinylpyrrolidone (NVP), maleic anhydride (MAH) and styrene (Sty) in the presence of **T1** [49]. In this case, the complex interplay of reactivity ratios means that the polymer composition is rich in MAH and NVP at one end of the chain, while being rich in MAH and Sty at the other end. Because of the symmetrical structure of **T1**, the final result is that the polymer flanks are rich in NVP–MAH, while the central domain is richer in Sty–MAH. This demonstrates the usefulness of combining RAFT and γ radiation to prepare one-pot gradient copolymers, in which a compositional gradient is evident along the polymer backbone.

Historically, one of the most common applications of γ radiation in polymer chemistry has been in grafting. This is due to the fact that γ radiation is an excellent method for generating radicals on polyolefin surfaces. Barner and co-workers have exploited this in the modification of SynPhase polypropylene lanterns for combinatorial chemistry applications [50,51]. In their first study, the lanterns were irradiated with

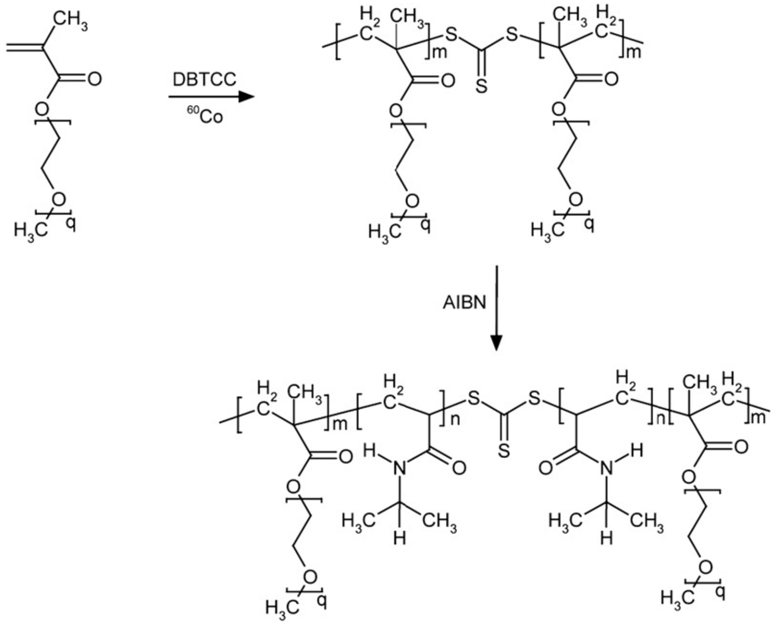


Fig. 6. Preparation of thermoresponsive comb polymers using γ-initiated RAFT polymerization. Poly(ethylene oxide) methyl ether methacrylate (MPEO-MA) was first polymerized under γ radiation in the presence of dibenzyl trithiocarbonate (**T1**). The macroRAFT agent thus prepared was then reacted with *N*-isopropylacrylamide in the presence of the thermal initiator azobisisobutyronitrile (AIBN). The resulting polymers had an ABA structure with a central block (“B”) of poly(*N*-isopropylacrylamide) flanked by two regions (“A”) of poly(MPEO-MA).

γ radiation in the presence of styrene and 2-phenylprop-2-yl phenyldithioacetate (**D6**) [50]. This resulted in the grafting of PSty onto the surface in a controlled fashion, whereby the grafting amount correlated with the concentration of **D6** and also the molecular weight of the free polystyrene formed in solution. Further work has examined the copolymerization of *m*-isopropenyl-α,α-dimethylbenzyl isocyanate with styrene under similar conditions (i.e. in the presence of **D6**, see Fig. 7) [51]. Again, a linear relationship was observed between the molecular weight of the free polymer and the grafting ratio. These isocyanate functional lanterns were subsequently demonstrated to be effective scavengers for benzyl amine, demonstrating the utility of γ-initiated RAFT for preparing high functionality materials. More recent work by Hill and co-workers has demonstrated the ability to graft poly(*tert*-butyl acrylate) onto a poly(ethylene-*co*-propylene) surface [52]. Again, the authors established that the grafted amount was dependent on the amount of RAFT agent (in this case 1-phenylethyl phenyldithioacetate, **D2**) added to the free solution, and that the molecular weight of the free polymer increased linearly with the conversion and also grafted mass. Importantly, these authors also demonstrated that the grafted P*t*BA could be hydrolyzed to give grafted PAA chains. Further, they also showed that the grafted polymers could be chain extended with styrene, indicating that the grafts were indeed “living”. Recently, Barner and co-workers verified that the grafting of styrene from cellulose via radiation-induced RAFT polymerization is controlled, i.e. the grafting of styrene is mediated via the RAFT agent [53]. In addition, they showed that grafted and non-grafted polystyrenes have almost the same (near theoretical) molecular weight and narrow

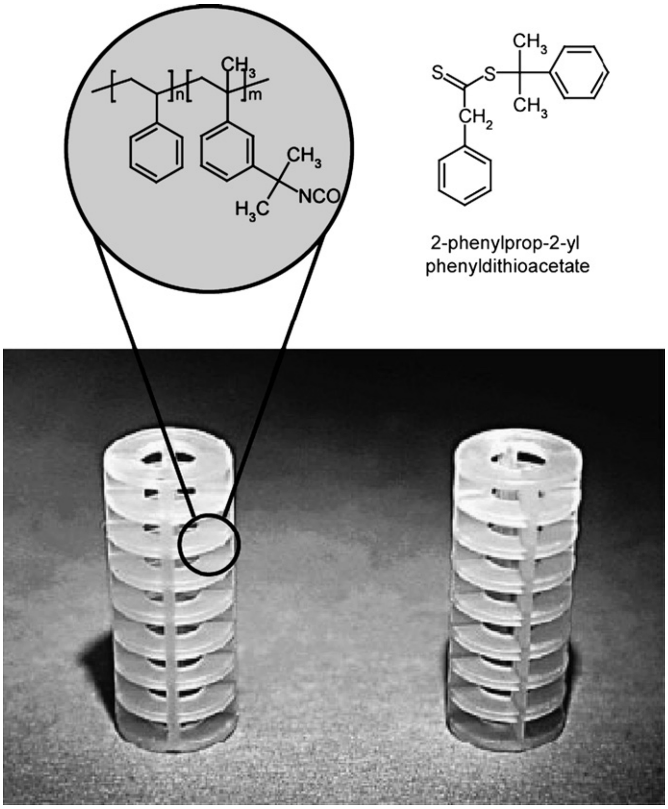


Fig. 7. Polypropylene SynPhase lanterns. These can be functionalized with isocyanate moieties by irradiating in the presence of a mixture of styrene and *m*-isopropenyl-α,α′-dimethylbenzyl isocyanate. The RAFT agent 2-phenylprop-2-yl phenyldithioacetate is added to ensure controlled growth from the lantern surface. The resulting chains possess pendant isocyanate groups. (Reproduced with kind permission from Ref. [51].)

polydispersity. RAFT polymerization was applied to radiation-induced graft polymerization of styrene from cellulose, using the chain transfer agent 2-phenylprop-2-yl phenyldithioacetate (**D6**) to mediate the polymerization. The cellulose was not functionalized prior to the grafting reaction. Grafted polystyrene chains were cleaved from the cellulose surface by acidic hydrolysis of the cellulose. The number-average molecular weight and polydispersity index of the grafted and the free (non-grafted) polystyrenes obtained under identical conditions were subsequently determined by size exclusion chromatography. It is clear from these results that γ radiation and RAFT polymerization are an extremely powerful combination for modifying the surface properties of polyolefins and other functional materials.

Allylic polymers are notoriously difficult to polymerize in a controlled fashion due to their tendency to form relatively stable radicals and to abstract hydrogen atoms. The polymerization of allyl azide is even more fraught, due to its relative thermal and UV instabilities. Bai and co-workers have recently reported the copolymerization of this useful allylic compound with styrene, MA and MMA in the presence of **X1** under γ radiation at 0 °C (see Fig. 8) [54]. The polymers formed were typically of narrow molecular weight distribution (PDI < 1.3), with incorporation of up to 18% of the allyl azide moieties in the final polymer chain. Moreover, the azide group was preserved, as demonstrated by FTIR observation of the characteristic peak at 2102 cm^{-1}. Azide functional polymers are of considerable interest, due to their ability to function as reaction intermediates and as biologically active additives. Importantly, the advent of the so-called ‘‘click’’ chemistry reactions such as the Huisgen 1,3-dipolar cycloaddition is also causing renewed interest in azide functional compounds [72]. Further work by Bai and co-workers on the copolymerization of acryloyl azide with MA has demonstrated that it is possible to prepare azide functional polymers via an alternative, all-acrylic route [55]. Again, the polymerization was conducted in the presence of **X1**, with the temperature kept at 0 °C. In this case the product was only observed to be stable at 2 °C: storage at higher temperatures (e.g., 20 °C) led to conversion of the pendant acryloyl azide groups into isocyanate groups (as observed using infrared spectroscopy). Such isocyanate groups are interesting in themselves (as shown above), and may be useful precursors to novel polyurethane or polyurea materials.

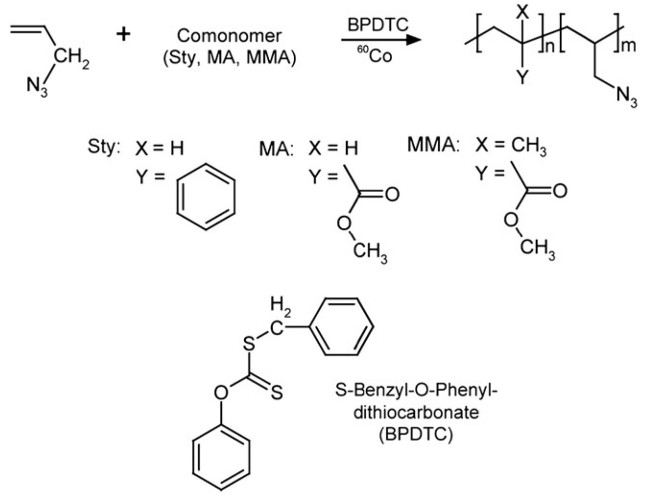


Fig. 8. Copolymerization of allyl azide with styrene, methyl acrylate or methyl methacrylate under a constant source of γ radiation, in the presence of *S*-benzoyl-*O*-phenyl dithiocarbonate (BPDTC, **X1**).

In addition to the utility of γ radiation for polymerizing monomers which are sensitive to elevated temperature, the approach is also extremely useful in applications where conjugation to a temperature sensitive entity, such as a protein or enzyme, is required. In recent work, Davis, Bulmus and co-workers have used a modified Ellman reagent to conjugate a RAFT agent onto bovine serum albumin (BSA) through the cysteine moiety [56]. This functionalized BSA was then exposed to low dose rate γ radiation in order to conjugate poly(ethylene glycol) acrylate (PEG-A) onto the protein via living radical polymerization (see Fig. 9). Characterization via MALDI-TOF MS and GPC was used to verify that the PEG-A was indeed attached to the protein. Further, MALDI-TOF MS and gel electrophoresis showed that by minimizing the dose rate, the proteins were largely unaffected by the radiation. Additional experiments on glucose oxidase also demonstrated that there was minimal loss of enzymatic activity after irradiation. This study confirms the usefulness of low temperature initiation via γ radiation, used in tandem with living radical polymerization for high technology applications such as bioconjugation.

It is evident that γ radiation, when used with living radical polymerization via RAFT, becomes an extremely powerful technique in polymer synthesis, surface modification and even in bioconjugation. Nevertheless, there are a number of other reports where other types of ionizing radiation have also been shown to be effective for initiating RAFT polymerization. These are discussed in more detail below.

4. Living polymerization under UV radiation via a RAFT mechanism: beyond thioiniferters

Ultraviolet radiation, like γ radiation, is a useful tool in applications such as surface grafting and crosslinking. While considerably more widely available than γ radiation, the number of reports which have used ultraviolet radiation to initiate RAFT polymerization is substantially fewer. This is likely due to the observed decomposition of some thiocarbonylthio moieties under UV radiation [73]. Nevertheless, the approach has still been used to prepare an interesting array of novel materials, a number of which are discussed in the following section.

The first report on UV-initiated RAFT polymerization examined the polymerization of Sty, MA and butyl acrylate (BA) in the presence of dibenzyl trithiocarbonate (**T1**) [57]. In each case, the polymerization proceeded with living characteristics, with the final polymer structure analogous to that formed in the corresponding experiments under γ radiation. The observed living behaviour was attributed to a reversible termination mechanism, wherein sequential homolytic cleavage of the C—S bond facilitates generation of both an initiating benzyl radical and a stable thiocarbonylthiyl radical. While the

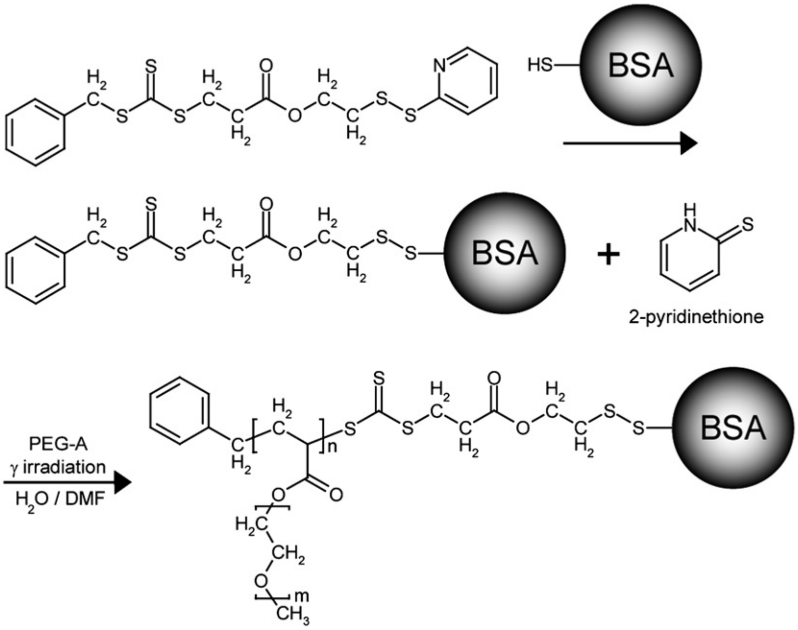


Fig. 9. Site-specific modification of bovine serum albumin (BSA) with a pyridyl disulfide terminated RAFT agent. This is then used for in situ polymerization of oligo(ethylene glycol) acrylate (PEG-A). DMF = *N*,*N*-dimethylformamide.

veracity or otherwise of this mechanism has not been formally proven, the observed experimental behaviour can equally well be explained in terms of a RAFT mechanism. Moreover, regardless of how the radicals are generated in the system, it is expected that they will undergo addition to the thiocarbonyl groups to some extent, resulting in at least some reversible addition–fragmentation behaviour. Subsequent work by Quinn et al. has demonstrated that, at least in the example of dithioester mediated polymerization under UV radiation, the polymerization proceeds via a RAFT, rather than reversible termination mechanism [58]. However, without unambiguous evidence either way it is not possible to assert with absolute certainty the origin of the experimental results in this first study [57]. Certainly, if a reversible termination mechanism was operative it may be that polymerization of MMA in the presence of **T1** would provide the answer. Under a reversible termination mechanism, such a system would display living characteristics, while if the polymerization proceeds via a RAFT mechanism the poor leaving group ability of the benzyl group with respect to the propagating methacrylyl chains would result in non-living behaviour.

In early work, Quinn et al. demonstrated the usefulness of 1-phenylethyl phenyldithioacetate (**D2**) for polymerization of styrene under ultraviolet radiation [58]. In this study, degradation of the dithioester moiety was observed over the duration of the reaction, and was found to be much more severe for dithiobenzoates (as opposed to phenyldithioacetates). Further, at high conversion, substantial broadening of the molecular weight distribution was observed, correlating with the destruction of the RAFT end group and the occurrence of other side reactions. Investigation was made into the nature of the degradation products, and it was determined that the phenyldithioacetate moiety most likely degrades through scission of the C–S linkage, followed by loss of carbon disulfide. This process results in benzyl radicals which may then abstract a hydrogen to form toluene as a degradation by-product or terminate with other radical species in the polymerization. Importantly, this limitation can be largely abrogated by using either fast polymerizing systems (where there is no sufficient time for dithioester degradation) or by using agents which are less susceptible to UV degradation. Notably, Barner and co-workers have recently explored the polymerization of acrylic acid in aqueous solution using *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (**T2**) as a RAFT agent [59]. In this example, high conversion (>50%) polymers were achieved with no obvious adverse effects on the molecular weight distribution, and extremely low PDI (in some cases < 1.1, see Fig. 10).

Subsequent explorations from the Pan group have examined the copolymerization of styrene and maleic anhydride in the presence of (1-ethoxycarbonyl)prop-1-yl dithiobenzoate (Fig. 2, **D8**) [60]. Initiation of this system using ultraviolet radiation led to the formation of alternating polymers, as is expected for this particular monomer system. The polymers produced were well defined, with narrow molecular weight distribution (PDI < 1.2) and molecular weight which agreed well with that from theory. While this particular study did not employ any additional photoinitiator (aside from the CTA itself), other studies have used the addition of a UV-labile compound to act as a source of initiating radicals. (Of course this is not required when the monomer itself is sensitive to UV radiation, as in the case of styrene.) Zhu and co-workers used the photoinitiator tetraethylthiuram disulfide along with the RAFT agent 2-cyano-prop-2-yl dithionaphthalate (**D5**) in the polymerization of styrene, and observed very good agreement between the theoretical molecular weight and that found experimentally [61]. Further, the authors were able to chain extend the macroCTA using either thermal initiation or

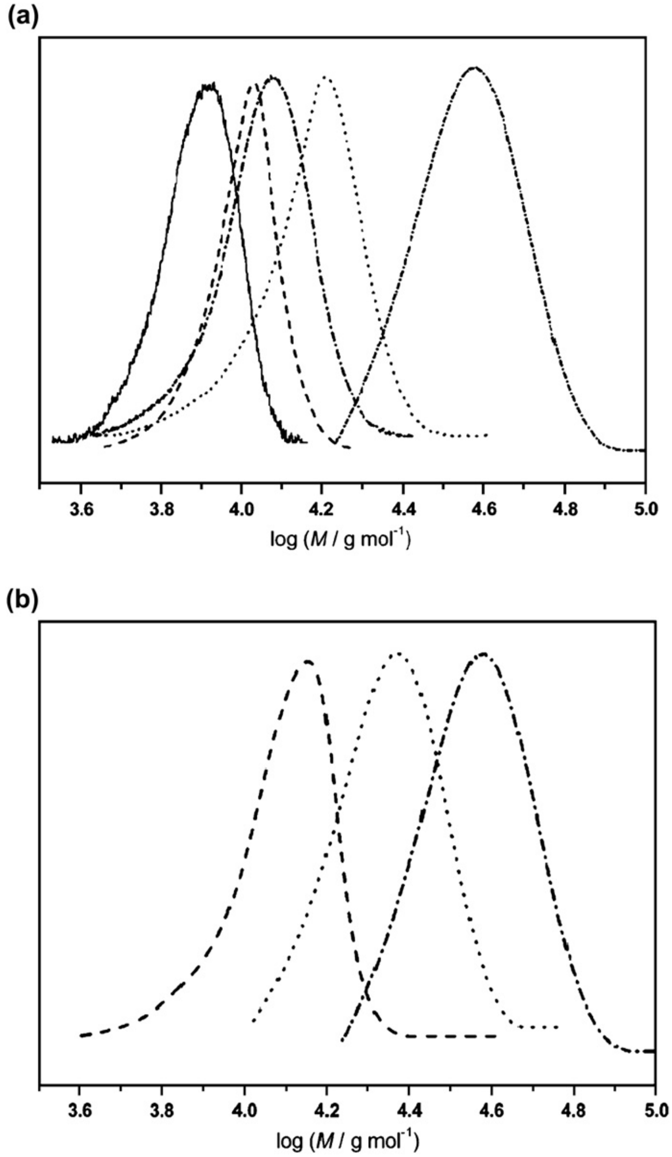


Fig. 10. (a) Evolution of the molecular weight distribution of poly(acrylic acid) with time: $[AA]_0 = 1.5\ \text{mol L}^{-1}$, $T = 25$ °C, [AA]/[TRITT] = 600, UV-irradiation at 365 nm, solvent = water, time = 90 min, 135 min, 165 min, 240 min, or 330 min (traces from left to right). (b) Dependence of the molecular weight distribution of poly(acrylic acid) on the ratio monomer/CTA using *S*,*S*-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (TRITT) as RAFT agent. $[AA]_0 = 1.5\ \text{mol L}^{-1}$, $T = 25$ °C, UV-irradiation at 365 nm, solvent = water, $[M]_0/[TRITT]_0 = 400$, 800, and 1000 (traces from left to right). (Reproduced with kind permission from Ref. [59].)

photoinitiation, though it should be noted that the thermal activation of the CTA produced narrower molecular weight distributions, presumably because of some loss of the dithioester moiety under UV radiation.

Building on the early work in the area by Quinn et al., Cai and co-workers conducted experiments using *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (**T2**) as a RAFT agent in the polymerization of MA [62]. Additionally, these authors added the photoinitiator (2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO)), allowing them to use only long wave radiation ($\lambda = 365-405$ nm), rather than full-wave radiation ($\lambda = 254-405$ nm). This greatly reduced destruction of the RAFT agent, by cutting off the wavelengths most detrimental to the thiocarbonylthio moiety. Further work by these authors demonstrated the application of 2-cyanoprop-2-yl 4-fluorodithiobenzoate (**D7**) along with TPO and visible radiation to prepare narrow molecular weight PMMA, and *S*′-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (**T3**) with TPO and long wave radiation to polymerize both MA and BA (and blocks thereof) [63]. These results demonstrate that by appropriate wavelength selection, the ability to use UV radiation in initiating RAFT polymerization can be further improved. Interestingly, the polymerization of BA in the presence of TPO and **T3** can also be performed under solar radiation, with very little loss of thiocarbonylthio moieties over the duration of the polymerization [64].

5. Plasma initiated living radical polymerization via RAFT

Plasma initiation, that is, the formation of radicals through a low pressure electrical discharge, is commonly used as a method for achieving very low concentrations of active species in a polymerizing system. Such a system is ideally suited in combination with RAFT, where the concentration of initiating radicals is best kept very low to ensure that the bulk of chains is initiated through the R group of the thiocarbonylthio compounds. A limited number of investigations have been carried out into the plasma initiated polymerization of MMA in the presence of 2-cyanoprop-2-yl dithionaphthalate (**D5**) [65,66]. In this system, the initiating radicals are formed solely from the MMA and not through the destruction of **D5**, as demonstrated by a series of control experiments with another monomer unable to be initiated through plasma initiation (styrene) [65]. The final PMMA formed possesses a narrow molecular weight distribution (typically < 1.4), and the theoretical molecular weight agrees well with that measured using gel permeation chromatography. The polymers could also be chain extended with either an additional segment of PMMA, or with PSty, confirming the living nature of the chain ends.

Importantly, further experiments on plasma initiation of RAFT polymerization have also been conducted in emulsion [66]. By applying the same initiation conditions to the emulsion polymerization of MMA, polymers were formed with slightly broader molecular weight distributions than those produced from bulk polymerization. Nevertheless, the polymers did still display living characteristics. It was also possible to polymerize octyl acrylate under the same conditions, and again excellent agreement was observed been theoretical and measured molecular weight [66]. While to date there have only been limited studies on these initiation conditions, the relative insensitivity of the RAFT agent to plasma initiation indicates that this methodology may be of some interest in a wider range of RAFT polymerization reactions.

6. Ionizing radiation as a kinetic tool

While all the examples discussed thus far have pertained to synthetic applications of ionizing radiation-initiated RAFT

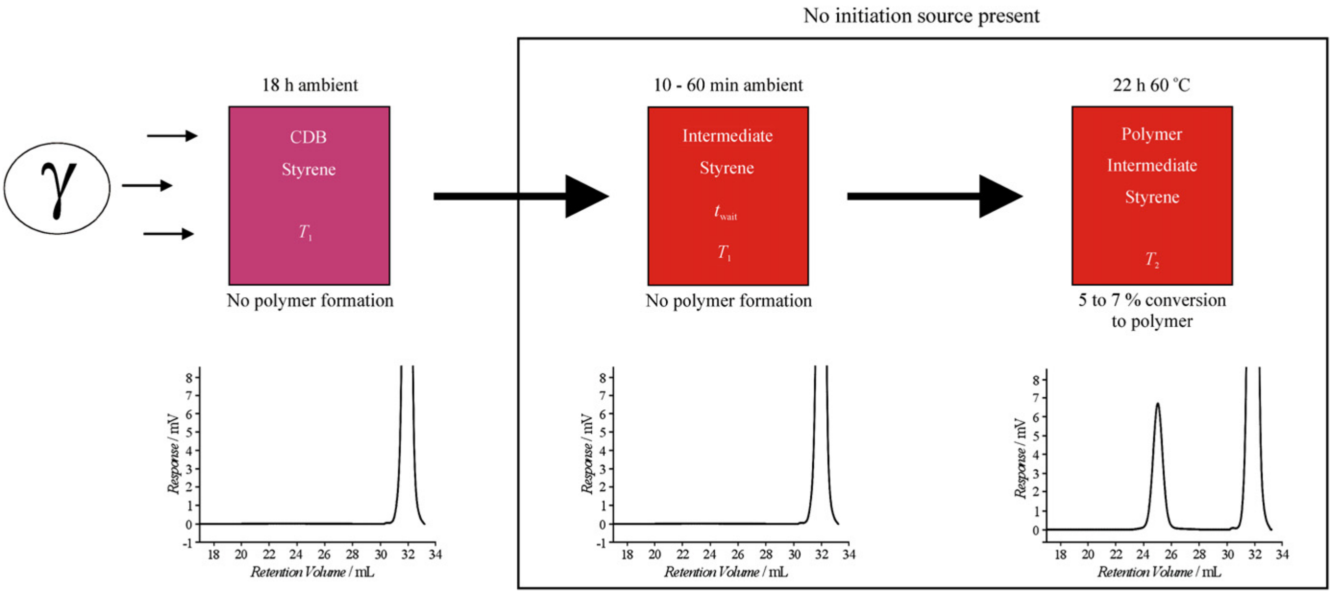


Fig. 11. The experimental procedure used to examine CDB-mediated styrene polymerizations for intermediate species formation. The lower part of the scheme gives examples of molecular weight distributions typical for each sequence step (the large peak at 32 min is due to monomer in the reaction mixture). (Reproduced with kind permission from Ref. [16].)

polymerization, the ability to access a constant source of initiation is also of considerable benefit in certain kinetic applications. Barner-Kowollik et al. used γ radiation to probe the lifetime of the intermediate radical formed during RAFT polymerization (see Fig. 11) [67]. These investigations stemmed from controversy over the fate of the intermediate radical formed during the initial chain transfer process, and the subsequent macromolecular chain transfer process [21–26]. Some authors contended that these radicals were able to undergo irreversible radical–radical coupling, which led to an apparent decrease in the rate of polymerization. Others held the view that the decrease in polymerization rate occurred because the intermediate radical was itself quite stable or because reversible termination of the intermediate radical was occurring. To investigate these observations, Barner-Kowollik et al. exposed a solution of 2-phenylprop-2-yl dithiobenzoate in styrene to γ radiation for a fixed time period. As expected, the polymerization under these conditions was severely retarded and no conversion was observed. However, upon elevating the temperature of this system to 60 °C *after γ radiation*, polymerization did occur. A control experiment without γ radiation confirmed that the origin of the polymer formed was not thermal initiation. As such, the undeniable conclusion was that the γ radiation-induced the formation of a species which was sufficiently long-lived, or able to act as a radical storage reservoir, so as to allow polymerization to be triggered later by an elevation of temperature. These experiments highlight the power of being able to switch off the source of initiation at a given point, a benefit which is unique to the use of ionizing radiation.

Gilbert and co-workers have also used γ radiation to probe the kinetic parameters associated with RAFT polymerization in emulsion [68,69]. These authors used γ relaxation experiments in which the source of initiation was cut off at a particular time and the decay of the polymerization thereafter measured. When using 2-phenylprop-2-yl phenyldithioacetate as the RAFT agent in the seeded emulsion polymerization of styrene, the time taken till complete cessation of polymerization after removal of the initiator was between 100 s and 200 s [68]. At first glance, these results appear to contradict those reported previously by Barner-Kowollik et al. However, the nature of the different RAFT agents used means that a far more stable intermediate radical is expected in the experiments reported by Barner-Kowollik, since the radical is situated in a benzylic position. As such, the two reports are completely consistent. Gilbert and co-workers use these γ relaxation experiments to obtain kinetic parameters from the system in question by assuming pseudo-bulk kinetics as an approximation to full compartmentalization/chain length dependent kinetics. Again, these studies demonstrate the usefulness of γ initiation in probing the kinetics of not only bulk, but also emulsion polymerization systems.

Further studies by Gilbert and co-workers have used γ relaxation experiments to examine the radical exit rate coefficient in the seeded emulsion polymerization of styrene mediated by xanthate transfer agents [69]. The authors observed that the exit rate increased with the amount of RAFT agent, and this was deemed to be consistent with both the characteristics of the RAFT agent and the standard transfer/diffusion mechanism for exit. Further, by combining the exit data with the steady-state rate under chemical initiation, the authors were able to determine entry rate coefficients. While there was no dependence of the entry rates with concentration of RAFT agent in the case of γ initiation (unless a high RAFT concentration was used), the case of chemical initiation showed that there was a decrease in the entry rate coefficients with the concentration of RAFT agent. Based on these observations, the authors were able to postulate that the xanthates used may indeed be surface active, and therefore frustrate the entry of radicals into the particle, leading ultimately to aqueous phase termination. These results further confirm that γ initiation is a powerful weapon in the elucidation of mechanistic and kinetic processes in RAFT polymerization.

7. Conclusions

The use of ionizing radiation as an initiation source in living radical polymerization has provided substantial synthetic and kinetic opportunities. The ability to conduct a host of polymerization reactions under very mild conditions (e.g., at room temperature) allows the opportunity to employ monomers and substrates which are highly temperature sensitive. Notable examples include the polymerization of azide functional monomers at 0 °C, and the polymerization of PEG-A in the presence of a protein supported RAFT agent. Moreover, the ease with which these initiation processes can be deactivated makes ionizing radiation a very useful tool in kinetic and mechanistic investigations.

Acknowledgements

The authors acknowledge support from the Australian Research Council in the form of an Australian Postdoctoral Fellowship (J.F.Q.), an Australian Professorial Fellowship (C.B.-K.) and a Federation Fellowship (T.P.D.). Funding through the Discovery Project Scheme is also acknowledged, along with support from the Particulate Fluids Processing Centre at the University of Melbourne.

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