Reversible Addition−Fragmentation Chain Transfer Polymerization Initiated with Ultraviolet Radiation

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Received March 19, 2002; Revised Manuscript Received June 5, 2002

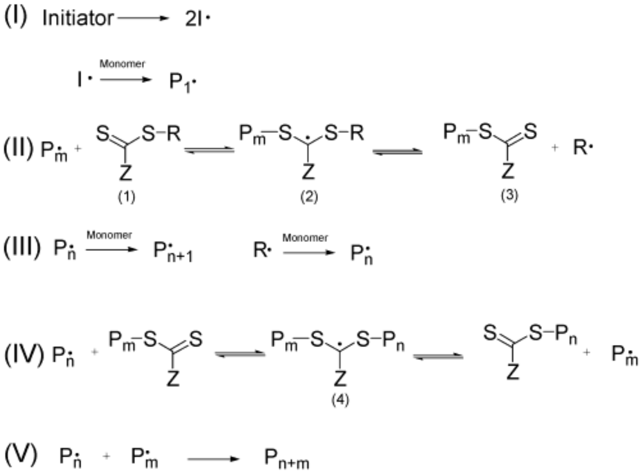
ABSTRACT: Styrene was polymerized under a source of ultraviolet radiation in the presence of certain thiocarbonylthio compounds. Use of 1-phenylethyl phenyldithioacetate (1-PEPDTA) produced well-defined polymers with molecular weights close to those predicted from theory, up to conversions of 30%. The mechanism of polymerization was examined and shown to proceed via reversible addition−fragmentation chain transfer, as opposed to reversible termination with a thiocarbonylthiyl radical. UV-induced decomposition of the dithioester moiety in 1-PEPDTA and 1-phenylethyl dithiobenzoate (1-PEDB) mediated RAFT polymerizations was followed using UV/vis spectrophotometry; 1-PEPDTA decomposed much slower than 1-PEDB. Analysis of the decomposition products of 1-PEPDTA with gas chromatography/mass spectrometry was used to elucidate a possible mechanism for its degradation, suggesting that both 1-phenylethyl and benzyl radicals are decomposition products.

Introduction

Reversible addition−fragmentation chain transfer (RAFT) polymerization is a versatile technique for the preparation of polymers with both low polydispersity and functionalizable end groups.[1−3] The technique employs thiocarbonylthio compounds in order to mediate the polymerization via a reversible chain transfer process. This leads to an equilibrium under which all the propagating chains grow proportionally with conversion. Considerable attention has been directed at the synthesis of complex architectures using RAFT[4−7] and also into the mechanism and kinetics of the process.[8−12] Recently, this group reported the synthesis of RAFT agents that can be applied at low temperatures in the polymerization of alkyl acrylates[13,14] and the use of such RAFT agents under a constant field of ^{60}Co γ-radiation.[15] This paper focuses on the application of those same RAFT agents with ultraviolet radiation to perform living polymerization.

Scheme 1 shows the widely accepted mechanism for reversible addition fragmentation chain transfer (RAFT) polymerization.[1] In essence, the mechanism relies on an initial release of initiating radicals through chain transfer (II) and a reversible addition fragmentation step (IV) through which irreversible termination events are minimized. During a particular transfer event, the propagating end of a chain is converted to a polymeric transfer agent, which can then undergo transfer itself, re-releasing the propagating radical. Through this equilibrium, chains convert from propagating radicals to polymeric transfer agents, meaning that they all grow incrementally with conversion. This process results in living radical behavior, characterized by a predictable, linear evolution of molecular weight with conversion, narrow molecular weight distribution, and pseudo-first-order kinetics.

Scheme 1. Schematic for Reversible Addition−Fragmentation Chain Transfer Polymerization



Scheme 2 shows the alternative explanation offered by Hong et al. for living behavior under both γ and ultraviolet radiation.[16,17] Under this scheme, radiation induces sequential homolytic cleavage of the carbon sulfur bond in the thiocarbonylthio compound, yielding a stable thiocarbonylthiyl radical. The other half of the molecule (R$^\bullet$) initiates polymerization, and the thus-generated propagating chains are then reversibly terminated by the stable radical. Hong et al. base this mechanism on the fact that the thiyl group of the Z−C(S)−S− is always bonded to the head of the monomer, indicating that the thiocarbonylthiyl radical must be “stable” (unable to initiate). However, this explanation cannot differentiate between the two mechanisms as polymers generated via the RAFT process will share the same structure. The reversible termination mechanism might also be operative in living polymerization under ultraviolet radiation using dithioesters, as ultraviolet radiation is effective in causing bond

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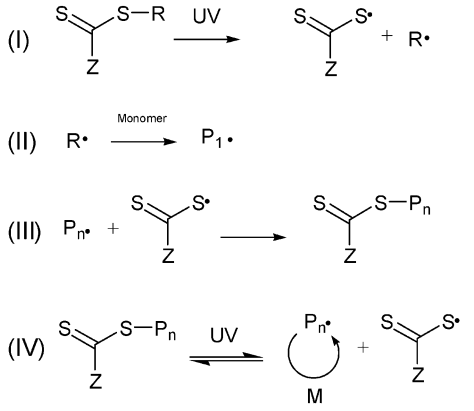
10.1021/ma0204296 CCC: $22.00

Scheme 2. Schematic for Reversible Termination Polymerization



cleavage in a variety of organic compounds. This paper seeks to reconcile which of the two mechanisms is imparting living characteristics to the polymerization. The reversible termination mechanism proposed by Hong et al. is quite different from the reversible *intermediate* termination discussed elsewhere by Barner-Kowollik and co-workers.[10,12]

Materials

1-Phenylethyl phenyldithioacetate (**1**) was synthesized and characterized using the method reported elsewhere by this group.[12] The inhibitor was removed from styrene (Aldrich, 99.9%, **2**) by percolating it over a column of activated basic alumina. Cumyl dithiobenzoate (CDB, **3**) and 1-phenylethyl dithiobenzoate (PEDB, **4**) were synthesized and characterized using the methods reported in the literature.[18,19] The inhibitor was removed from methyl methacrylate (MMA, Aldrich, **5**) by percolating it over a column of activated basic alumina. Monomers and RAFT agents are shown in Scheme 3.

Experimental Section

Living Polymerization of Styrene. Two solutions of 1-PEPDTA in styrene were prepared gravimetrically (17.1 and 9.5 mmol L^{-1}). Bulk polymerizations were conducted in 3 mL aliquots in glass sample vials, capped with rubber septa, and deoxygenated by purging with nitrogen gas for 10 min each. Duplicates were taken to account for variations in wall thickness of the glass vials. The samples were placed in a UVP CL-1000L ultraviolet cross-linker ($\lambda_{max} = 365$ nm, 60 μWcm^{-2}) at an angle of 30° to ensure irradiation through the ampule. Samples were taken at 2, 4, 8, 12, 16, 24, 48, 72, 96, and 120 h. The conversion of each sample was determined gravimetrically after drying, initially in a fume hood and then in a vacuum oven at 30 °C for 24 h.

Mechanistic Studies Using Methyl Methacrylate. Solutions of CDB and 1-PEDB in monomer were prepared gravimetrically (4.1 mmol L^{-1} CDB in MMA and 4.0 mmol L^{-1} PEDB in MMA). Bulk polymerizations were conducted in 3 mL aliquots in glass sample vials, capped with rubber septa, and deoxygenated by purging with nitrogen gas for 15 min each. The samples were placed in a UVP CL-1000L ultraviolet cross-linker ($\lambda_{max} = 365$ nm, 60 μWcm^{-2}) at an angle of 30° to ensure irradiation through the ampule. Samples were taken after 1, 2, 3, 4, 6, and 8 h. The conversion of each sample was determined gravimetrically after drying initially in a fume hood and then in a vacuum oven at 30 °C for 24 h.

Molecular Weight Analysis. Molecular weight distributions were measured by size exclusion chromatography (SEC) on a Shimadzu modular system, comprising an autoinjector, a Polymer Laboratories 5.0 μm bead size guard column (50 × 7.5 mm), followed by three linear PL columns (10^5, 10^4, and 10^3 Å), and a differential refractive index detector. The eluent was tetrahydrofuran (THF) at 40 °C with a flow rate of 1 mL min^{-1}. The system was calibrated using narrow polystyrene standards ranging from 500 to 10^6 g mol^{-1}.

UV/vis Spectrophotometry of Polymerizing Systems. Solutions of 1-PEPDTA and 1-PEDB in styrene were prepared gravimetrically (7.8 and 8.1 mmol L^{-1}, respectively). Bulk polymerizations were conducted in 4 mL quartz cuvettes, capped with rubber septa, and deoxygenated by purging with nitrogen gas for 10 min each. Spectra were recorded on a Cary 350 UV/vis spectrometer both before and after deoxygenation to account for concentration variations induced by evaporation during the deoxygenation process. The samples were then placed in a UVP CL-1000L ultraviolet cross-linker at an angle of 30° to ensure irradiation through the ampule. The sample was removed and a spectrum recorded at 1, 2, 3, 4, 6, and 8 h. A series of identical concentration samples were prepared in the same way and run with the cuvettes. These were sampled at the same time intervals for determination of (a) conversion and (b) molecular weight distribution.

Analysis of Decomposition of 1-Phenylethyl Phenyldithioacatetate. Analysis of 1-phenylethyl phenyldithioacetate was performed by irradiating the compound in a deoxygenated benzene solution for 64 h. The resultant mixture was then air-dried for 2 h in order to remove the bulk of the benzene and then analyzed using a Shimadzu QP 5000 gas chromatograph/mass spectrometer with a DB5 column 30 m × 0.25 mm. Program conditions: 35 °C for 5 min and then heated to 250 °C at a heating rate of 5 °C/min.

Results and Discussion

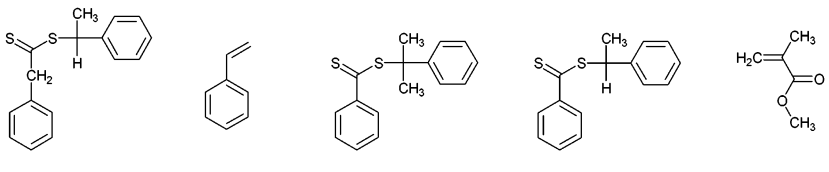
Living Polymerization. Living polymerization of styrene (**2**) was observed under ultraviolet radiation at 365 nm, using 1-phenylethyl phenyldithioacetate (**1**) as the RAFT agent and without the addition of any thermal or photoinitiator. This living behavior is demonstrated in Figure 1, which shows the linear evolution of the number-average molecular weight with conversion, up to a reaction conversion of 16%. This figure also shows that adherence of experimental molecular weight to theoretical molecular weight is excellent. This indicates that the generation of initiating radicals is low with respect to the concentration of RAFT agent, meaning that close to 100% of the chains have terminal units generated from the RAFT agent itself. The potential source of these initiating radicals was investigated later in the study.

The kinetics of living free radical polymerization are first order with respect to the monomer concentration and adhere to the general rate equation

$$\frac{d[M]}{dt} = -k[M] \tag{1}$$

where [M] is the monomer concentration, t is the time, and k is the pseudo-first-order rate constant. Pseudo-first-order kinetics were confirmed for 1-PEPDTA mediated polymerization of styrene, with both the high and low concentrations studied showing first-order behavior (see Figure 2). This indicates that the steady state radical concentration is roughly constant over the duration of the polymerization. Importantly, polymerization of styrene under ultraviolet radiation with no added 1-PEPDTA proceeded at a comparable rate, indicating that radicals can also be formed from the monomer as well as the RAFT agent. There is little evidence of retardation in 1-PEPDTA mediated polymerization of styrene—that is, the reaction proceeds at approximately the same rate regardless of the concen-

Scheme 3. 1-PEPDTA, Styrene, CDB, PEDB, and Methyl Methacrylate



1 **2** **3** **4** **5**

tration of 1-PEPDTA. This is consistent with previously reported results using analogous RAFT agents.[10,20]

The molecular weight distributions remain quite narrow in the early stages of the polymerization (see Figure 1 (M_w/M_n) and Figure 3). This agrees with the observations in thermal and γ initiated RAFT polymerization. However, at higher conversions there is some loss of control over the molecular weight distribution when ultraviolet radiation is used as a source of initiation. This is demonstrated in Figure 4, which shows that for reaction times that are longer than 48 h the molecular weight distribution begins to lose its narrow, symmetrical character and to broaden considerably. At these longer times the polymer also loses its characteristic yellow color and becomes clear, indicating that the chromophoric dithioester moiety is destroyed and that the products of the degradation reaction are largely colorless. This would also account for the broadening of the distribution, because as the dithioester moiety in any particular chain is destroyed, that chain loses its ability to propagate further. This results in chains being "left behind" and the distribution broadening. De Brouwer et al. found that irradiating polymers prepared via RAFT with ultraviolet radiation resulted in little initial color change, with colorless polymer only obtained after column chromatography.[21] However, his experiment used a dithiobenzoate terminated polymer solution that had not been deoxygenated.

Later distributions show three key features when compared to those at shorter reaction times: a low molecular weight peak/shoulder, the main peak, and a high molecular weight shoulder. As mentioned above, the low molecular weight shoulder emerges from the degradation of the dithioester end group of the polymer, giving a portion of "dead" polystyrene that is unable to continue growing. The high molecular weight shoulder may have emerged from one of three origins. First, it may be the product of bimolecular termination. Second, as the polymerization is glassy after 72 h, it may have

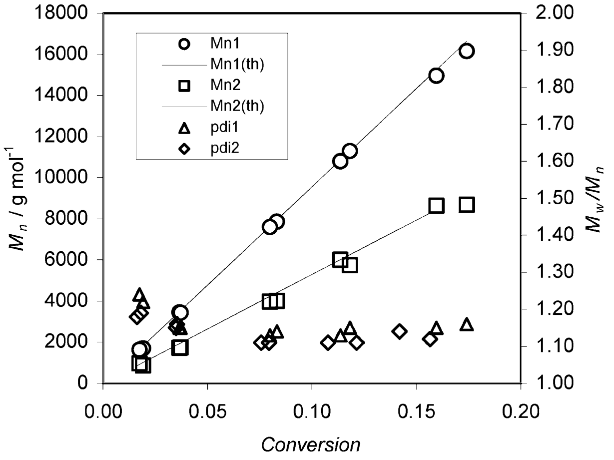


Figure 1. Number-average molecular weight vs conversion. Styrene in bulk. [1-PEPDTA] = 9 mmol L^{-1} (○); [1-PEPDTA] = 17 mmol L^{-1} (□). T = 42 °C.

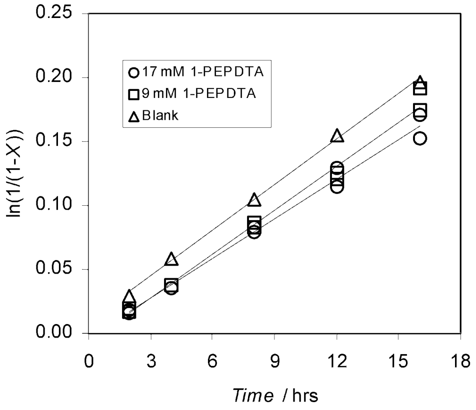


Figure 2. Pseudo-first-order plot. Styrene in bulk. [1-PEPDTA] = 9 mmol L^{-1} (○); [1-PEPDTA] = 17 mmol L^{-1} (□). T = 42 °C.

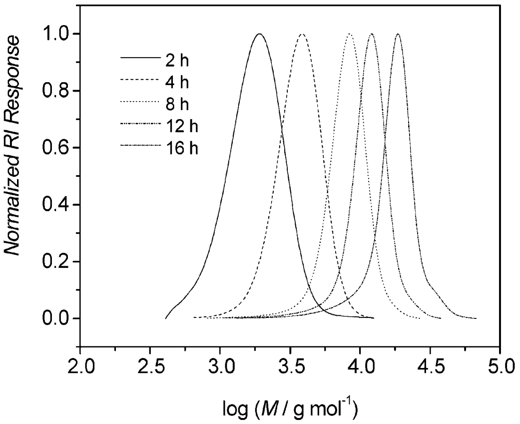


Figure 3. Evolution of molecular weight distribution with time. Styrene in bulk. t = 2−16 h. [1-PEPDTA] = 9 mmol L^{-1}. T = 42 °C.

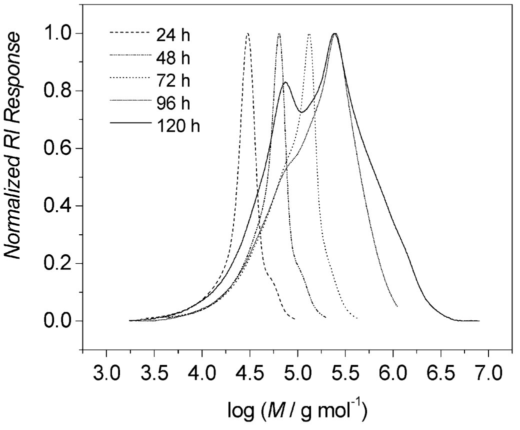


Figure 4. Evolution of molecular weight distribution with time. Styrene in bulk. t = 24−120 h. [1-PEPDTA] = 9 mmol L^{-1}. T = 42 °C.

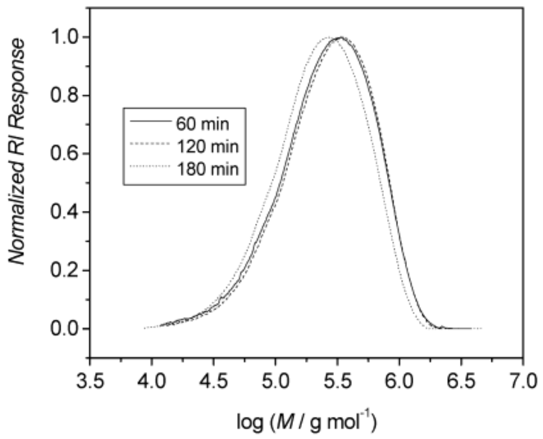


Figure 5. Mechanistic investigation of UV initiated LFRP. Evolution of molecular weight distribution with time. MMA in bulk. [1-PEDB] = 4.0 mmol L^{-1}. T = 42 °C.

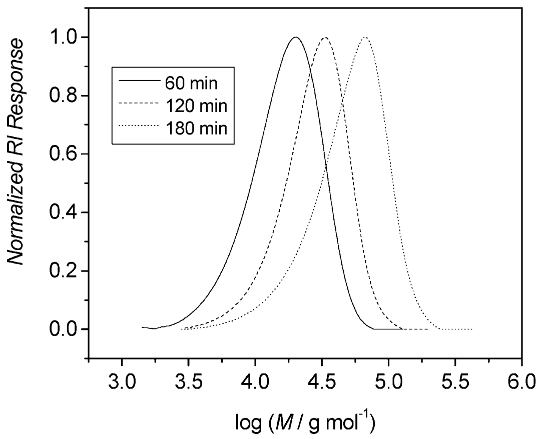


Figure 6. Mechanistic investigation of UV initiated LFRP. Evolution of molecular weight distribution with time. MMA in bulk. [CDB] = 4.1 mmol L^{-1}. T = 42 °C.

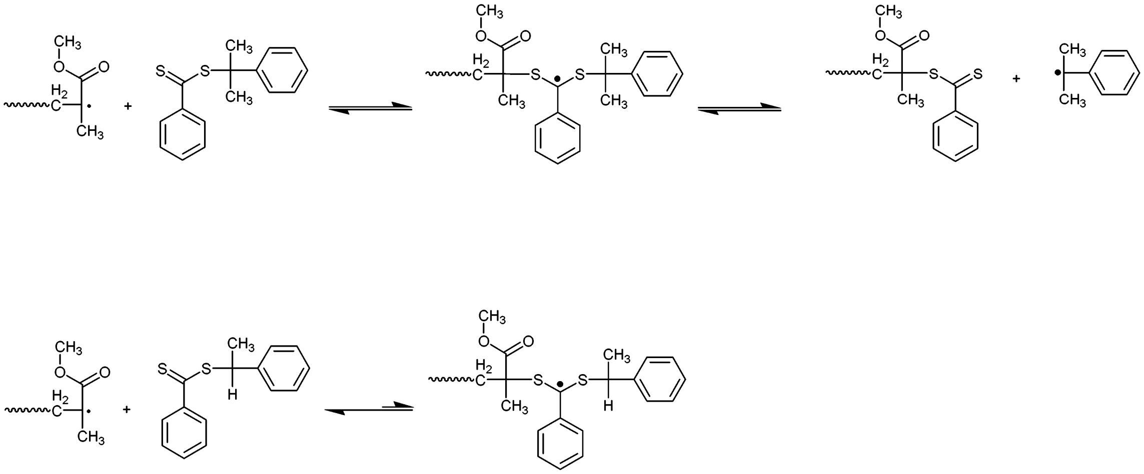
originated from branching reactions that have occurred in this glassy stage of the polymerization. Third, the molecular weight increase may have emerged through intermediate termination reactions such as those suggested by de Brouwer et al.[21] In any case, the narrow polydispersity is clearly lost at higher conversions and higher total doses of ultraviolet radiation.

Mechanism of Polymerization. Methyl methacrylate (**5**) was polymerized under ultraviolet radiation in the presence of two thiocarbonylthio compounds with different R groups to distinguish between the RAFT and reversible termination mechanisms discussed earlier.[22] If the RAFT mechanism is efficacious, then the identity of the R group of the thiocarbonylthio compound is critical to the success of the polymerization. If the R group is not a good leaving group relative to the propagating radical, then the propagating radical will simply fragment off the thiocarbonyl again. Therefore, the RAFT agent will be effectively inert in the polymerization, and the resulting molecular weight distributions will be broad and not shift to higher molecular weight with increasing conversion. On the other hand, if the mechanism of the polymerization involves reversible termination, then the identity of the R group will have no effect on the polymerization, if it is a good initiating species. In this study, 1-phenylethyl dithiobenzoate (1-PEDB, **4**) and 2-phenylprop-2-yl (cumyl) dithiobenzoate (CDB, **3**) were used; if the origin of living behavior is RAFT, only CDB should give living characteristics with MMA. If the mechanism is reversible termination, both PEDB and CDB should give living behavior with MMA, as both 1-phenylethyl and cumyl radicals have been shown to initiate polymerization of methyl methacrylate.[23,24]

Polymerization of methyl methacrylate in the presence of 1-phenylethyl dithiobenzoate yielded no evidence of living behavior. Even though the conversion is increasing with time, Figure 5 clearly shows that the polymer formed is high molecular weight initially (M_n = 135 000 g mol^{-1}) and that the molecular weight does not increase with increasing conversion. However, polymerization of methyl methacrylate in the presence of cumyl dithiobenzoate yields a molecular weight distribution that shifts to higher molecular weight with increasing conversion (Figure 6). This clearly indicates that R determines whether the polymerization is living.

Scheme 4 shows the initial transfer reactions in both PEDB and CDB mediated polymerizations of methyl methacrylate. In both cases, the propagating methacryloyl radical adds to the thiocarbonyl group of the dithioester. However, when R = 1-phenylethyl, the methacryloyl group will fragment preferentially, yielding back the original RAFT agent and methacryloyl radicals. Under this scenario, the bulk of propagating chains are initiated by ultraviolet radiation (i.e., continuously throughout the polymerization) rather than through the R group of the RAFT agent. Therefore, the polymerization is uncontrolled. In the case where the

Scheme 4. Effect of R Group in Reversible Addition Fragmentation Chain Transfer



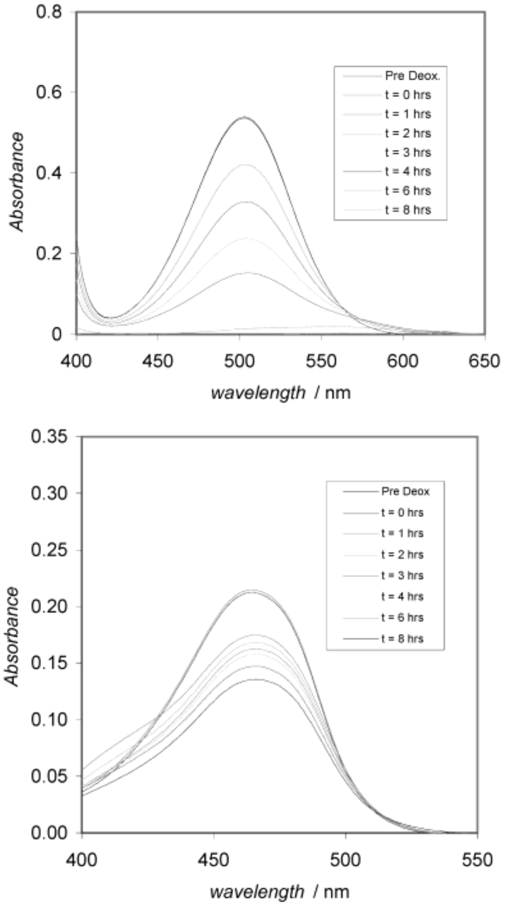


Figure 7. (a) UV/vis spectra of 1-PEDB in polymerization of styrene. [1-PEDB] = 4.2 mmol L^{-1}. $t = 0-8$ h. $T = 42$ °C. (b) UV/vis spectra of 1-PEPDTA in polymerization of styrene. [1-PEPDTA] = 4.2 mmol L^{-1}. $t = 0-8$ h. $T = 42$ °C.

leaving group is a cumyl radical (a comparable leaving group to the methacryloyl radical), there is an early release of initiating species into the polymerization, and the bulk of chains are initiated through the RAFT agent. The result is that all the chains start growing at around the same time in the polymerization. This (along with the reversible addition−fragmentation equilibrium) leads to the vast majority of the chains having approximately the same kinetic chain length at any given extent of reaction. The resulting polymerization is living.

You et al. recently reported the living polymerizations of styrene, methyl acrylate, and butyl acrylate in the presence of dibenzyl trithiocarbonate (DBTC) under ultraviolet radiation.[17] To explain this living behavior, these authors appealed to a reversible termination or *iniferter* mechanism. However, this explanation is inadequate. When radicals are generated in the system, whether by cleavage of the carbon sulfur bond or by any other bond breaking reactions, some radicals will add to the thiocarbonyl group of the DBTC, just as they do in conventional RAFT polymerization. DBTC induces living behavior in thermal polymerization of styrene, and AIBN initiated polymerization of methyl acrylate.[4] Therefore, using radiation to generate the radicals is unlikely to lead to a completely different mechanism of polymerization; radicals will still add to the thiocarbonyl group.

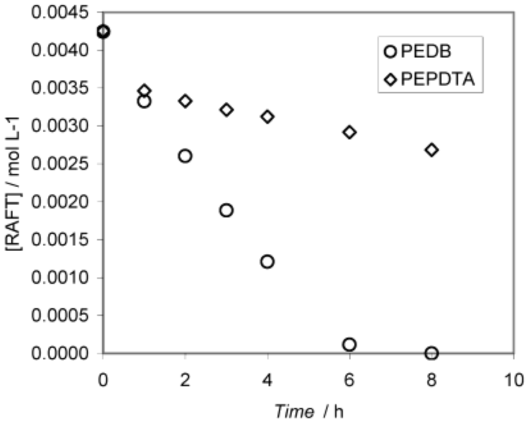


Figure 8. Decomposition of 1-PEDB and 1-PEPDTA with time followed by UV/vis spectrophotometry. $[\text{1-PEPDTA}]_0 = [\text{1-PEDB}]_0 = 4.2$ mmol L^{-1}. $t = 0-8$ h. $T = 42$ °C.

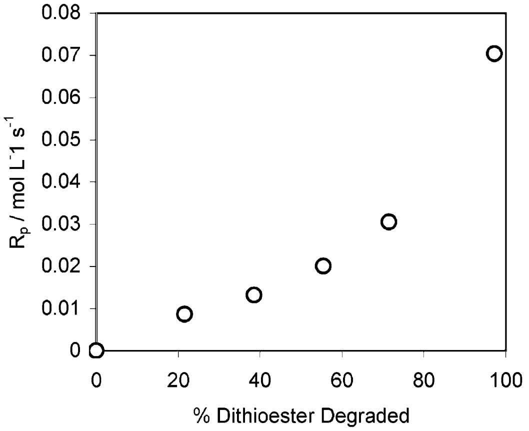


Figure 9. Rate of polymerization vs % dithioester degraded. Styrene in bulk. $[\text{1-PEDB}]_0 = 4.2$ mmol L^{-1}.

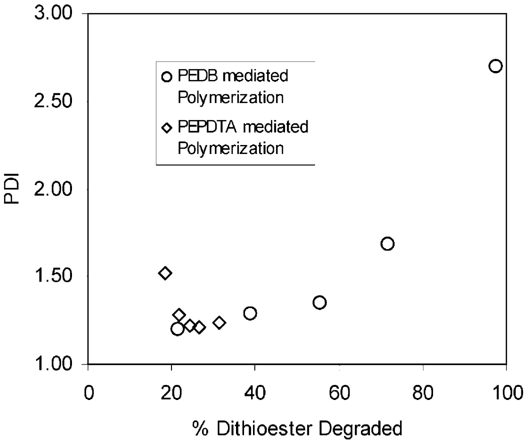
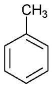
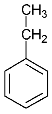
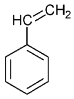
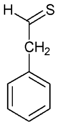
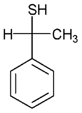
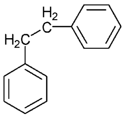
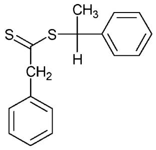


Figure 10. Broadness of distribution (PDI) vs % dithioester degraded. Styrene in bulk. $[\text{1-PEPDTA}]_0 = [\text{1-PEDB}]_0 = 4.2$ mmol L^{-1}.

The fact that the reversible termination mechanism fails in explaining living behavior in the presence of dithioesters is not surprising. There is little evidence to account for the stability of the reversibly terminating species generated in this case, other than the fact that it is always connected to the head of the monomer. However, as mentioned in the Introduction, this is not sufficient evidence alone, as polymers formed via RAFT will have an *identical* structure. Further, the reversible termination mechanism does not account for the fate of radicals generated by bond cleavage in the monomer, since cleavage events may occur in both the monomer and RAFT agent. Methyl methacrylate was shown to homopolymerize under this particular light source, and

Table 1. Species Formed via UV Irradiation of 1-PEPDTA

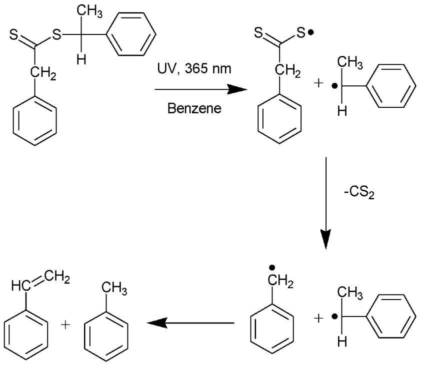
Retention Time (min)	Molecular Weight (Da)	Possible Species
4.58	92	
8.18	106	
9.33	104	
15.77	136	
15.85	138	
17.78	182	
43.72	272	

thus the probability that sequential homolytic cleavage will take place *exclusively* at the C−S bond is low, given the much larger concentration of monomer. The release of these additional monomer derived radicals into the system would be expected have a significant effect on the molecular weight distributions, if the reversible termination mechanism was operative. The latter part of this publication will suggest that cleavage of the C−S bond does take place under ultraviolet radiation, but rather than assist in the livingness of the polymerization, the cleavage products further degrade and thereby decrease the control exerted over the polymerization by the RAFT process.

Mechanism of Transfer Agent Decomposition and Initiation. As the dithioester compounds used in this study are highly colored, the decomposition of the dithioester moiety in the polymerizing system can be followed by UV/vis spectrophotometry. Figure 7a,b shows the decrease in the intensity of the UV/vis spectra of 1-phenylethyl dithiobenzoate (**4**) and 1-phenylethyl phenyldithioacetate (**1**) with time. 1-Phenylethyl phenyldithioacetate shows a large decrease in the absorbance during the first hour of the polymerization and thereafter an almost linear decrease. This larger initial decrease may originate from one of two phenomena. First, the initial dithioester may be more susceptible to UV degradation than the polymeric species. Second, and more likely, the initial RAFT agent may have a slightly different extinction coefficient than the polymeric one (due to changes in the conjugation within the chromophore). This means that the concentrations determined with time may be slightly underestimated. This may also occur when 1-phenylethyl dithiobenzoate is used as the RAFT agent but may be not as pronounced due to 1-PEDB having a much larger extinction coefficient than 1-PEPDTA.

Figure 8 shows the concentration of the two RAFT agents with time of irradiation. Both RAFT agents

Scheme 5. Proposed Mechanism for the Decomposition of 1-PEPDTA under UV Radiation



degrade, but 1-PEDB decays much faster; it is almost 100% degraded after 6 h. Because of the well-documented retardation effects in dithiobenzoate polymerization,[9,12,13,19] the conversion after this time is also quite low. On the other hand, 1-PEPDTA degrades much more slowly, and the concentration has little effect on the rate of polymerization. 1-PEPDTA is therefore a far superior RAFT agent to 1-PEDB for polymerization under ultraviolet radiation. When higher concentrations of 1-PEPDTA are used, the percentage loss of dithioester is quite small at short reaction times, and the distributions are not affected until much later in the reaction (see Figures 3 and 4). Unfortunately, using higher concentrations of 1-PEDB does not overcome this problem, as it induces a higher level of concentration-dependent retardation, requiring longer reaction times. Only when the 1-PEDB is largely destroyed does the polymerization start to proceed at an appreciable rate (see Figure 9). This increase in rate may be due to either destruction of the retarding species or introduction of extra radicals from the dithiobenzoate decomposition.

Figure 10 shows the correlation of polydispersity index with the percentage of dithioester moiety degraded. The effect is most clearly seen when 1-PEDB is used as the RAFT agent due to its much faster decomposition. The graph shows that as the dithioester moiety is broken down, the polydispersity indices increase, which is the key limitation of ultraviolet initiated RAFT. However, as mentioned above, appropriate selection of the RAFT agent and concentration can reduce the effects of this degradation. This is also demonstrated in Figure 10, with the PDI values for 1-PEPDTA mediated polymerization remaining low (<1.25) up to 30% degradation.

To probe the mechanism of dithioester decomposition more closely, a solution of 1-phenylethyl phenyldithioacetate in benzene was prepared, deoxygenated, and irradiated under UV lamps ($\lambda_{\max} = 365$ nm). Residual benzene was then evaporated, and the residue was analyzed by gas chromatography/mass spectrometry. Table 1 shows the proposed identity of the major species in the chromatogram.

The presence of styrene, ethylbenzene, and toluene in the chromatogram suggests that both benzyl and phenylethyl radicals may be formed in the decomposition of 1-phenylethyl phenyldithioacetate under ultraviolet radiation. The benzyl radical may then abstract a hydrogen atom from the phenylethyl radical, giving styrene and toluene as the products (see Scheme 5). This reaction may also occur between two phenylethyl radicals, producing styrene and ethylbenzene as the products. These compounds are all present in the residue. Further, the presence of 1,2-diphenylethane also suggests that benzyl radicals are generated in the decomposition reaction. Importantly, both benzyl and 1-phenylethyl radicals are able to initiate polymerization. Therefore, under ultraviolet radiation, 1-phenylethyl phenyldithioacetate may act both as a source of initiating species and as a transfer agent.

There is also evidence of other products in the residue formed by scission of the (C═S)−S bond in the transfer agent (1-phenylethanethiol and phenylthioacetaldehyde). The presence of these species suggests that the degradation of the transfer agent under ultraviolet radiation does not proceed exclusively via one mechanism but may occur in at least two different ways. Nevertheless, the production of at least some initiating species from the decomposition of the RAFT agent is evident.

There is still a large amount of 1-phenylethyl phenyldithioactetate left in the reaction mixture after irradiation. This is significant because, although the RAFT agent decomposes under ultraviolet radiation, this decomposition occurs at low enough levels to leave enough transfer agent for the RAFT process to proceed. This verifies the result obtained via UV/vis measurement of the polymerizing system.

Conclusion

Reversible addition−fragmentation chain transfer polymerization was performed using styrene as the monomer and 1-phenylethyl phenyldithioacetate as the transfer agent under ultraviolet radiation at 365 nm. The polymerization was shown to proceed with living characteristics (linear evolution of molecular weight with conversion, narrow molecular weight distribution, and good adherence to theoretical molecular weight). Significant broadening of the distribution was observed at long irradiation times, probably due to decomposition of transfer sites at the end of the polymer chain and/or branching reactions. The origin of this living behavior was determined to be RAFT rather than reversible termination. Decomposition of dithioester end groups in the polymerizing system was also followed using UV/vis spectrophotometry, and the decomposition of 1-PEDB proceeded much faster than 1-PEPDTA. A mechanism was proposed for the decomposition of 1-PEPDTA under UV which yielded phenylethyl and benzyl radicals, both capable of initiating polymerization. Evidence for the mechanism was provided using GC/MS analysis of residue from the irradiation of the neat transfer agent.

Acknowledgment. The authors gratefully acknowledge the financial support of the Australian Research Council (Australian Postgraduate Award, JQ), the Cooperative Research Centre for Polymers, Uniqema (ICI), and Mimotopes Ltd.

Supporting Information Available: Tables of RAFT polymerization of styrene, control experiments of styrene, UV mechanistic studies of methyl metacrylate, and UV degradation studies of styrene. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0204296