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Photoinitiated Block Copolymer Formation Using Dithiocarbamate Free Radical Chemistry

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ABSTRACT: Photoinitiated block copolymer formation from macromolecules terminated with dithiocarbamate end groups was studied. In most experiments results consistent with those reported by Otsu et al. were observed. A previously unreported side reaction, leading to decomposition of the dithiocarbamate end groups, was observed. The extent of this reaction appeared to depend on the stability of the incipient macroradical formed during photolysis. Statistical mixtures of homopolymers and block copolymers were formed during the addition of methyl methacrylate to poly(styrene) and styrene to poly(methyl methacrylate). The dithiocarbamate radical did not readily initiate the polymerization of ethyl acrylate or butyl acrylate, thus relatively clean block copolymers formed when these monomers were added to polystyrene.

Introduction

Most addition polymers with complex architectures, i.e., blocks, stars, etc., are prepared by living anionic, cationic, or group-transfer polymerization techniques. The control of architecture by free radical techniques has been a synthetic goal for many years because there are a large variety of monomers that polymerize by free radicals that do not do so via ionic techniques. In general, the high reactivity and nonselectivity of free radicals make it difficult to achieve block copolymers with the same level of control and purity as can be obtained by using the anionic, cationic, and group-transfer processes. "Living" free radical chemistry based on the photolysis of "iniferter" dithiocarbamate compounds has been described as an attractive technique for preparing simple block copolymers and more complex polymer architectures.[1] This report describes our results with this technique.

Experimental Section

Tetraethylthiuram disulfide was obtained from Aldrich and recrystallized from methanol prior to use. Xylenyl dithiocarbamate (XDC) and benzyl dithiocarbamate were prepared as described by Otsu in ref 6. Monomers were purified by removing inhibitor with an appropriate column obtained from Scientific Polymer Products followed by fractional distillation. Magnetically stirred crimp-top borosilicate glass bottles were used as polymerization vessels. The contents were sparged with argon and then sealed. Photolysis reactions were conducted with a 250-W sunlamp behind a 3-cm-thick infrared filter of glass plates with a constant flow of water between them. The temperature of the polymerization samples behind this barrier was maintained at 20–25 °C. Preparation of dithiocarbamate-containing end-capped homopolymers was done thermally at 60 °C in bottles under argon with tetraethyldithiuram disulfide as the

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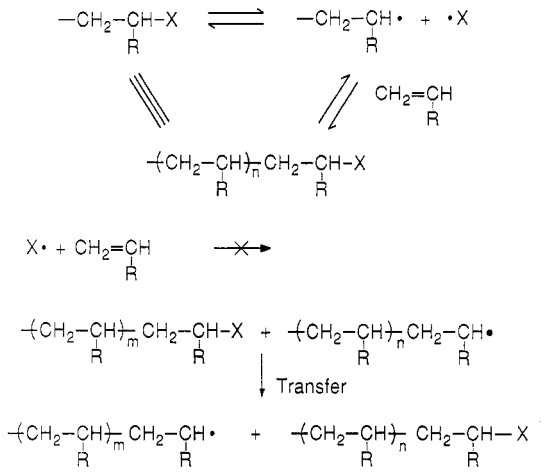
Scheme I
Free Radical "Iniferter" Process



initiator. Polymers were recovered by precipitation of the reaction solution into methanol and drying. The resulting polymer was then purified by redissolving in THF and reprecipitating into heptane, drying, redissolving, and reprecipitating into methanol. This procedure effectively removed any unreacted initiator or monomer. The presence of residual initiator and the concentration of end groups were determined as described previously[2] by UV analyses and by 300-MHz solution proton NMR. GC/mass spectrometer results were obtained by injecting a 0.5-μL sample from the head space of a sealed polymerization vessel into a 100 °C port, with a 30 °C oven, with single-ion monitoring at 38, 76, and 78 (peaks for CS_2). Polymer number-average molecular weights (M_n) were determined by size-exclusion chromatography (SEC) in THF using 10^6–10^3 Å nominal pore ultrastyragel columns. The columns were calibrated with narrow weight distribution polystyrene standards, and the results are plotted as polystyrene equivalent molecular weights.

Results and Discussion

Telechelic dithiocarbamate-functionalized polymers of styrene or methyl methacrylate were prepared via thermal free radical initiation with tetraethylthiuram disulfide. Transfer to initiator has been reported previously.[3-5] NMR and UV analyses confirmed the presence of the dithiocarbamate end groups. Otsu[1] has shown that photolysis of the active chain end group (the benzylic end for poly(styrene)) can lead to chain extension or block copolymer formation as illustrated in Scheme I. In chain extension experiments that added styrene monomer onto dithiocarbamate-terminated poly(styrene), our results were similar to those reported. An increase in molecular weight proportional to photolysis time was observed. These results are shown in Figure 1 for a sample with an initial $\bar{M}_n$ of 8400 and photolysis times of 1–5 h. In addition, we observed minimal broadening of the molecular weight distribution (determined by SEC) during the chain extension process (Figure 2). In a separate experiment, for a poly(styrene) sample with an initial $\bar{M}_n$ of 19 000, we observed that the $\bar{M}_n$ increased linearly until the experiment was discontinued after 29 h (Figure 3). At longer photolysis times, the molecular weight distribution broadened slightly from 1.51 (initially) to 2.15 after 29 h of exposure.

The appearance of such "clean" SEC traces suggested to us that this chain extension could be operating by something other than a free radical mechanism. A "nonallowed" photocycloaddition step would give the desired chain extension. The thermal [3,3]-sigmatropic reaction and intermolecular Cope reaction are allowed. However, we did not observe chain extension by a thermal reaction. We confirmed the free radical nature of the process by doing the photolysis chain extension in the presence of an efficient free radical chain transfer agent, dodecyl thiol. The results are shown in Figure 4 and are explained by the conventional transfer step in Scheme II, which is the origin of the low molecular weight poly(styrene) fraction. In addition to the chain-transfer results, free radical inhibitors such as *p*-benzoquinone and cupric chloride shut down the chain-extension reaction completely.

The photochemical chain extension of dithiocarbamate-terminated poly(methyl methacrylate) (PMMA) appears to be a more complicated process. Results for molecular weight growth versus time are plotted in Figure 5. Similar nonlinear results have been previously reported.[6] During the course of these and other experiments involving the photolysis of PMMA polymers, we observed the formation of a yellow color and bubbles in the reaction solutions. Head space GC/MS analysis indicated that CS_2 was formed. Experiments using the small

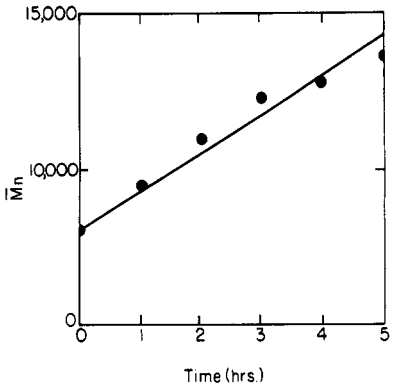


Figure 1. Increase in $\bar{M}_n$ (SEC) with photolysis time for styrene added to poly(styrene). A sample solution of 1.5 g of dithiocarbamate-capped poly(styrene) ($\bar{M}_n$ = 8400), 1.5 g of styrene, and 7 g of toluene was divided equally and placed into five polymerization vials. These solutions were irradiated and precipitated at the given times.

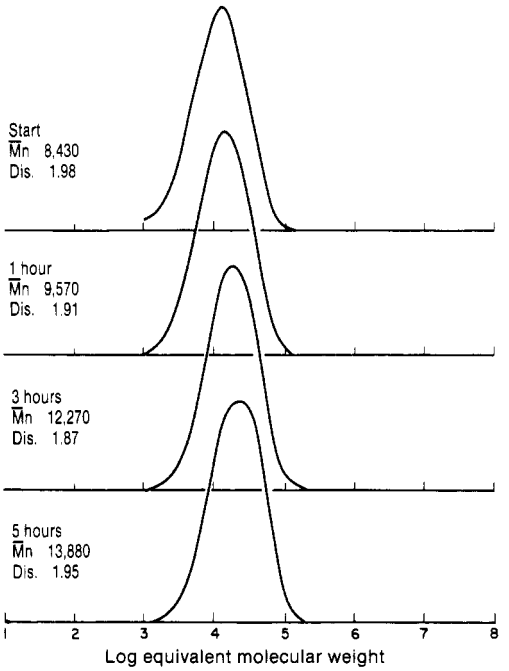


Figure 2. SEC traces for dithiocarbamate-terminated poly(styrene) ($\bar{M}_n$ = 8400) samples that were chain extended with styrene and precipitated at hourly intervals.

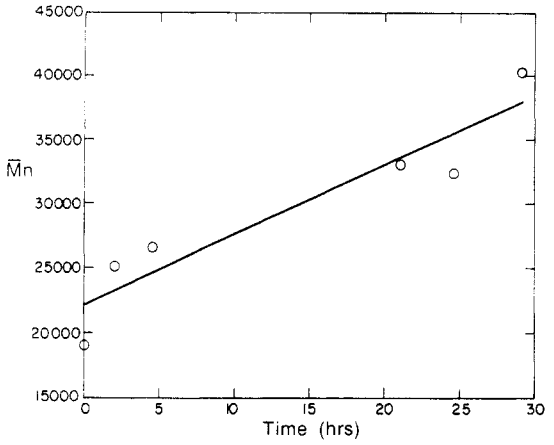


Figure 3. Increase in $\bar{M}_n$ (SEC) with photolysis time for styrene added to poly(styrene). A sample of 2 g of dithiocarbamate-capped poly(styrene) ($\bar{M}_n$ = 19 000), 4 g of styrene, and 18 g of toluene was divided equally into five polymerization vials. These solutions were irradiated and precipitated at the given intervals.

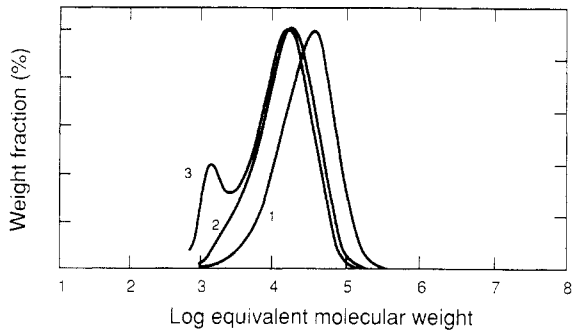
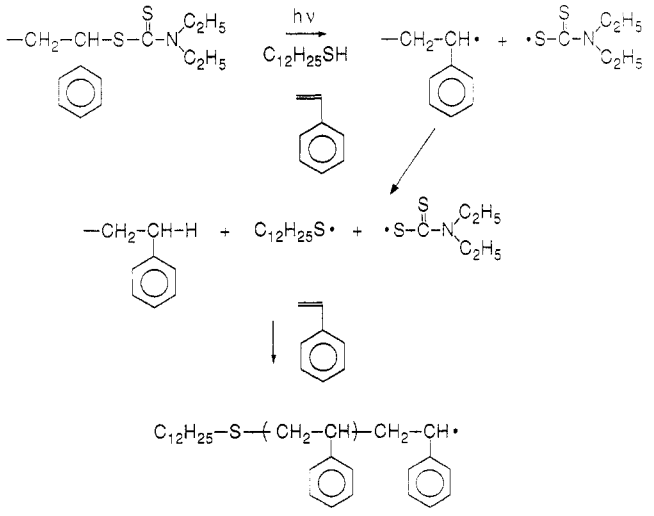


Figure 4. SEC traces for chain-extended dithiocarbamate-terminated poly(styrene) with various amounts of dodecyl thiol added as chain-transfer agent. The polymerization solutions contained 0.5 g of poly(styrene), 1.0 g of styrene, 2 g of toluene, and (1) 0 wt %, (2) 3.3 wt %, and (3) 6.6 wt % of thiol.

Scheme II
Chain Transfer to Dodecyl Thiol



molecule difunctional xylenyl dithiocarbamate in methyl methacrylate showed that the amount of CS_2 observed increased linearly with photolysis time. A similar experiment with styrene also showed CS_2 evolution, but at a much lower level. A control experiment with the xylenyl dithiocarbamate initiator in toluene gave an ion response in the experiment similar to the styrene results.

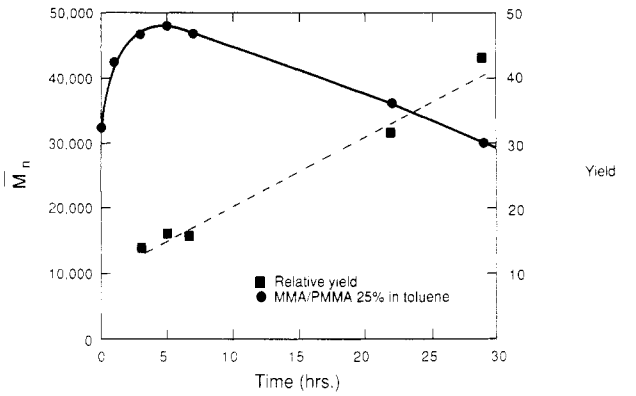


Figure 5. Percent conversion versus time and $\bar{M}_n$ versus time for dithiocarbamate-terminated poly(methyl methacrylate) chain extended with methyl methacrylate. A sample solution of 2 g of poly(methyl methacrylate), 4 g of methyl methacrylate, and 18 g of toluene was prepared and divided into separate vials. These solutions were irradiated and precipitated at the given intervals.

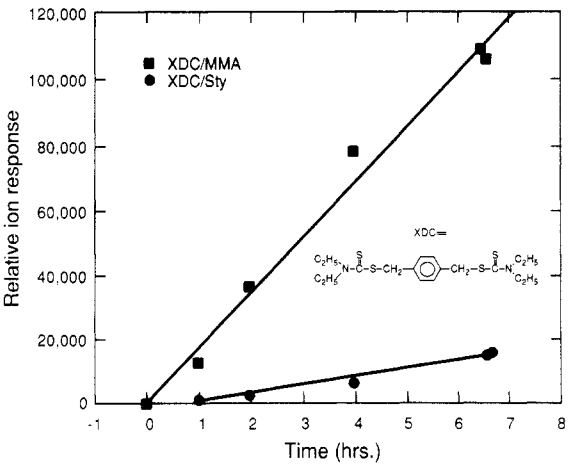
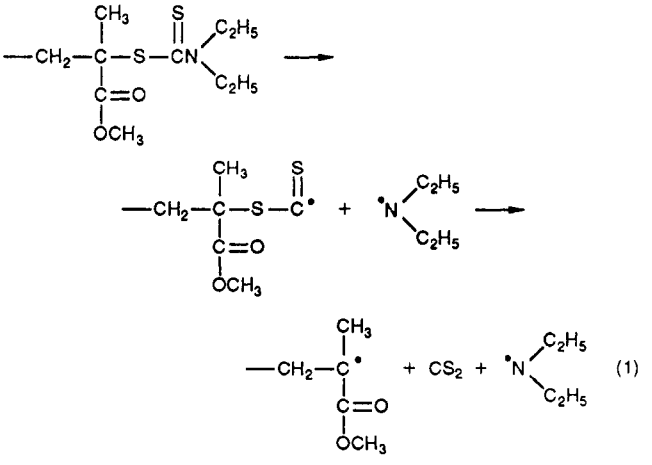


Figure 6. GC/MS results plotted as the relative ion response (concentration) versus photolysis time for 0.5 mmol of XDC in either 1.5 g of methyl methacrylate or styrene.

These results are plotted in Figure 6. The decomposition of the dithiocarbamate occurring during the photoinitiation process would lead to loss of the living nature of the chain end.

We propose a photochemical cleavage of the thiocarbonyl–nitrogen bond and subsequent elimination of CS_2



(1)

as the decomposition pathway (eq 1). For poly(styrene) the more stable benzylic radical apparently enhances the

Table I
Block Copolymer Results

polymer/monomer	conditions[a]	yield[b]	% starting polymer recovered	% polymer 2nd monomer recovered	% block recovered	starting $\bar{M}_n$ (MWD)	final $\bar{M}_n$ (MWD)
1. PSty/MMA	43% toluene, 2:1, 20 h	85%	5	28 (30)[c]	67 (65)	21 000 (1.60)	37 000 (1.62)
2. PMMA/Sty	43% toluene, 2:1, 20 h	32%	10	15 (20)	75 (72)	36 000 (1.63)	29 000 (4.14)
3. PSty/MMA	31% benzene, 6:1, 6 h	20%			79[d] (71)	83 000	192 000
4. PMMA/Sty	50% benzene, 15:1, 1 h	7%			78[d] (74)	64 000	294 000
5. PSty/butyl acrylate	33% THF, 1:1, 18 h	43%		0		21 000 (1.60)	33 000 (1.61)

[a] Concentration is (monomer + polymer) divided by (monomer + polymer + solvent). Ratio is the monomer to polymer ratio (weight) in the reaction vessel. [b] Yield equals (polymer collected − starting polymer)/monomer added × 100. [c] Numbers in parenthesis are calculated yields based on equal reactivities of both polymer radical and dithiocarbamate radical for initiating the second monomer. [d] Reference 2.

photochemical cleavage of the benzylic–dithiocarbamate bond. The diethylamino radical (diethylamine was also detected in the GC/MS experiments) may initiate the homopolymerization of methyl methacrylate and account for the nonlinear molecular weight growth in Figure 4. Unfortunately, the GC/MS results did not allow us to quantify the extent to which this detrimental side reaction occurs.

We have prepared a number of block copolymers by this technique. Some examples are summarized in Table I. When we blocked methyl methacrylate onto poly(styrene) and styrene onto poly(methyl methacrylate), we were able to separate the block copolymer from the starting reactive homopolymer and the homopolymer of the second monomer using selective dissolution with cyclohexane and acetonitrile.[7] The efficiency of the separation was confirmed by the NMR of the separated fractions. In both cases, essentially statistical mixtures of the block copolymer and homopolymers were isolated (entries 1 and 2 in Table I). These results indicate that the dithiocarbamate radical is as effective as the macroradical in polymerizing the added monomer. Even though we have worked at somewhat lower monomer to polymer feed ratios than those previously reported, our results appear to contradict the living nature of the iniferter concept. Our data appear consistent with previously published data (entries 3 and 4 in Table I).[2]

We have observed that with acrylate monomers the blocking selectivity appears to improve. For example, we were unable to initiate the thermal polymerization of butyl acrylate or ethyl acrylate with tetraethyldithiuram disulfide or the photochemical polymerization of the same monomers with either benzyl dithiocarbamate or xylenyl dithiocarbamate. These results indicate that the acrylate function is inactive to the dithiocarbamate radical. Photochemical blocking of butyl acrylate to poly(styrene) appears to yield pure block copolymers (Table I, entry 5). However, at this time we have not found a solvent combination that would separate block copolymers and homopolymers completely if they were formed in the photochemical blocking step.

Summary and Conclusions

Our study of the living free radical dithiocarbamate photochemical blocking polymerization chemistry has shown that this technique can be used to prepare block copolymers. We have identified a side reaction that suggests a fundamental limitation to the living nature of these systems. Our results indicate that statistical mixtures of block copolymer and homopolymer are formed by this chemistry with styrene and methyl methacrylate. We have also observed that acrylate monomers show better selectivity and may lead to relatively high-purity block copolymers.

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