

Notes

A Facile Synthesis Route to Thiol-Functionalized α,ω -Telechelic Polymers via Reversible Addition Fragmentation Chain Transfer Polymerization

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Introduction

A general synthetic methodology to thiol-functional telechelic polymers has been developed. This method, based on the use of difunctional chain transfer agents (CTAs) with reversible addition fragmentation chain transfer (RAFT) polymerization, is a straightforward and versatile procedure which produces well-defined α,ω -thiol telechelic polymers in one step directly from the products isolated after polymerization.

Telechelic polymers (α,ω -functionality) are generally defined as relatively low molecular weight macromolecules with selectively positioned functional groups at both termini of any given chain. Such polymers have been thoroughly studied within the realm of many applications including precursors in the synthesis of block copolymers, formation of polymer networks, and use as cross-linking agents and as compatibilizers in polymer blends.¹ While the synthesis of telechelic polymers containing functional groups such as hydroxy,² carboxylic acid,³ and amine⁴ have been well documented in the literature, far less attention has been given to telechelics which contain a thiol functionality at the chain ends. Thiols or mercaptans are widely used in many areas of chemistry and materials science by exploiting the specific interaction of the thiol with metals such as gold, silver, and cadmium. In addition, advances in technology in the areas of biochemistry and microelectronics have further increased the need for a straightforward approach to thiol-functional materials.⁵ Although there are many reports of polymers bearing an ill-defined number of mercapto groups,⁶ only a few examples have been reported for the preparation of well-defined thiol-containing polymers, most of which address macromolecules that contain a thiol at only one end, i.e., mono- or heterofunctional telechelics. In most cases, thiols are incorporated at the terminus of a polymer by coupling a protected thiol with preexisting functionalities at the end of the polymer chain. Trollsas et al. employed this approach in which they reported the synthesis of monofunctional thiol telechelics based on Sangers reagent (2,4-dinitrofluorobenzene). Although this method is carried out under mild conditions, it is

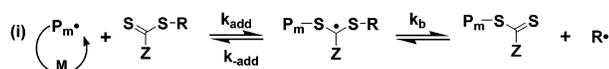
limited by the availability of hydroxyl-functionalized telechelics as precursors for the reaction.⁷ Carrot and co-workers extended the use of Sangers reagent to include functional initiators for atom transfer radical polymerization (ATRP) and ring-opening polymerization which resolved the limitation of hydroxyl-functionalized telechelics.⁸ Even so, by employing such an approach, one is limited to the synthesis of monofunctional thiol telechelics. To access α,ω -dithiol telechelics, an alternate route must be considered. In this regard, few accounts exist in the literature for the preparation of difunctional thiol telechelics.^{1c} For example, Kim and co-workers recently reported the synthesis of α,ω -thiol-functionalized polystyrene telechelics by anionic polymerization upon the reaction of α,ω -dilithiopolystyrene with ethylene sulfide. While the authors report functionalization yields of greater than 98 mol %, the procedure requires the stringent conditions of anionic polymerization. A milder approach involving controlled radical polymerization (CRP) would be desirable since CRP methods generally require less stringent conditions than anionic polymerization (most reactions can be carried out under inert atmosphere at mild temperatures). In addition, CRP offers more versatility in the types of functional monomers that may be polymerized under CRP conditions.

Reversible addition fragmentation chain transfer polymerization (RAFT) is an extremely versatile, controlled free radical polymerization technique for the synthesis of well-defined polymer architectures with narrow polydispersity.⁹ The RAFT process is applicable to a wide range of monomers and can be performed under a broad range of conditions.¹⁰ The RAFT technique relies on a degenerative transfer mechanism in which a chain transfer agent (CTA) (typically a thio-carbonylthio compound $S=C(Z)-SR$) reacts with either an initiator-derived primary radical or a propagating polymer chain (P^*), forming a new CTA and eliminating R^* , which is able to reinitiate the polymerization. The transfer of the CTAs between dormant and active chains effectively controls the polymerization (Scheme 1). The nature of the RAFT mechanism allows one to produce polymers that carry dithioester end groups which upon reduction yields macromolecules bearing a thiol functionality at the end of the polymer chain.¹¹ Thus, by employing a bifunctional CTA similar to that shown in Scheme 2, one has a facile route for the synthesis of polymers with α,ω -dithiol telechelic functionality, i.e., $HS-(P)_n-SH$. Polymers bearing α,ω -thiol functionality are of particular interest for the investigation of multiply bound polymer chains (MBPCs) in which both ends of the polymer are surface-bound (surface attached "polymer loop"), in contrast with the traditional singly bound polymer brush.¹² Such systems have the capability to form surface-bound polymer loops on a substrate and may exhibit drastically different interfacial properties (e.g., adhesion, wetting, biocompatibility, etc.) in

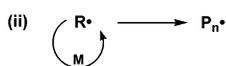
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Scheme 1. The RAFT Mechanism

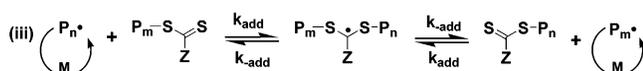
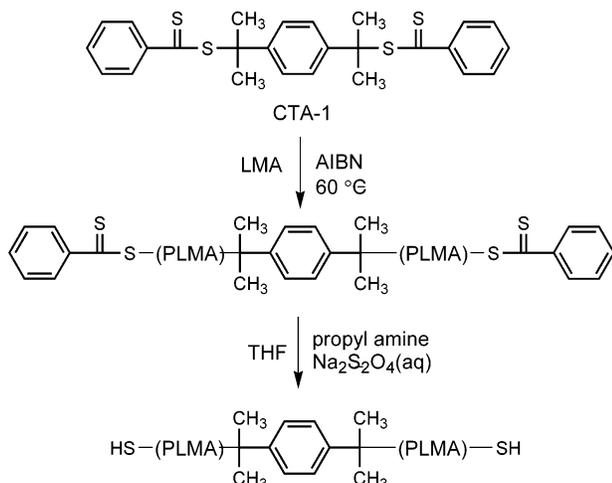
Chain Transfer



Reinitiation and Propagation



Chain Equilibrium

Scheme 2. Schematic Representation for the Synthesis of α,ω -Thiol Telechelics from a Difunctional CTA

comparison to single-tethered polymer systems.¹³ In this note, we report a straightforward method for the preparation of α,ω -dithiol telechelics as demonstrated by the synthesis of poly(lauryl methacrylate), poly(methyl methacrylate), and poly(styrene) containing thiol functionalities at both ends of the polymer chain. This is accomplished through the use of difunctional CTAs and the RAFT technique which yields the difunctional thiol telechelics in one reaction following polymerization. With minimal purification, α,ω -dithiol telechelics are achieved after the quantitative cleavage of the dithioester via aminolysis. Improved thermal properties were observed in the absence of the dithioester end group. The approach presented in the current work demonstrates an extremely facile route to α,ω -thiol telechelics via controlled radical polymerization.

Experimental Section

Materials. Reagent chemicals were purchased from Aldrich and used without further purification unless otherwise indicated. 1,4-Diisopropenylbenzene was purchased from TCI. Tetrahydrofuran (THF) used in synthesis was distilled from sodium benzophenone. Styrene and methyl methacrylate (MMA) were passed through a column of activated basic alumina to remove the inhibitor, distilled, and stored at -20 °C. Lauryl methacrylate (LMA) was diluted with hexane and washed three times with an aqueous solution of sodium hydroxide (5 wt %) followed by three times with distilled water. LMA was dried over MgSO₄ and passed through a column of neutral alumina prior to solvent removal. LMA was stored at -20 °C. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol.

1,4-Bis(2-(thiobenzoylthio)prop-2-yl)benzene (CTA-1).¹⁴ A mixture of dithiobenzoic acid (6.12 g, 0.0397 mol) and

1,4-diisopropenylbenzene (3.00 g, 0.0189 mol) in carbon tetrachloride (50 mL) was heated at 75 °C for 20 h. The volatiles were removed under reduced pressure, and the residue was triturated with 1:2 diethyl ether/hexanes to isolate the product as a pink solid (41.1%). ¹H NMR, δ (ppm): 1.99 (12H, s); 7.33 (m, 4H); 7.47 (m, 2H); 7.50 (s, 4H) and 7.86 (m, 4H). ¹³C NMR: δ (ppm) in CDCl₃: 226.92, 146.31, 142.63, 131.74, 128.12, 126.60, 126.34, 56.29, 28.10. Elemental analysis calculated for C₂₆H₂₆S₄: C, 66.91; H, 5.61; S, 27.48. Found: C, 66.70; H, 5.56; S, 27.19.

1,4-Bis(thiobenzoylthiomethyl)benzene (CTA-2).¹⁴ Phenylmagnesium bromide was prepared from bromobenzene (5.94 g, 0.038 mol) and magnesium turnings (0.965 g, 0.0397 mol) in dry THF (75 mL). The solution was heated to 40 °C, and carbon disulfide (2.88 g, 0.038 mol) was added dropwise over 15 min while keeping the reaction temperature at 40 °C. α,α -Dibromoxylene (5 g, 0.0189 mol) in 25 mL of dry THF was then added dropwise over 15 min to the resulting dark brown solution. The reaction temperature was maintained at 40 °C for 1.5 h. Ice water (150 mL) was added, and the organic products were extracted with ether (3 \times 30 mL). The combined organic phase was washed with water and brine and dried over anhydrous magnesium sulfate. Removal of the solvent yielded a red solid. The solid was recrystallized from ethanol to yield the product as a bright red solid (4.295 g, 55.2%). ¹H NMR, δ (ppm): 4.60 (4H, s); 7.34–7.60 (6H, m); 8.00 (4H, m). ¹³C NMR: δ (ppm) in CDCl₃: 227.6, 144.64, 134.63, 132.63, 132.47, 129.62, 128.35, 126.89, 41.74. Elemental analysis calculated for C₂₂H₁₈S₄: C, 64.35; H, 4.42; S, 31.23. Found: C, 64.27; H, 4.32; S, 31.03.

General Procedure for Polymerization. All polymerizations were performed in a Schlenk apparatus under homogeneous conditions. The polymerizations were initiated by addition of AIBN. Solutions of the respective monomer, initiator, and RAFT agent were prepared in Schlenk tubes fitted with septa and a stir bar. The mixtures were thoroughly deoxygenated by 3–5 freeze–pump–thaw cycles, backfilled with nitrogen, and placed in a thermostated water bath at preset temperature. At specific time intervals, aliquots were removed and quenched by lowering the temperature to 0 °C. Unreacted monomer was removed under reduced pressure at ambient temperatures or by precipitation and centrifugation. The resulting residue was analyzed directly by gel permeation chromatography (GPC).

Reduction of the Dithioester Termini by Aminolysis.

The α,ω -dithioester end-capped polymers were dissolved in THF containing a few drops of aqueous sodium bisulfite (Na₂S₂O₄). The reaction mixture was purged of oxygen by either bubbling with N₂ for 15 min or by three successive freeze–pump–thaw cycles. Propylamine (degassed) was then added in excess via syringe, and the reaction was stirred overnight under N₂. Upon the addition of the propylamine, an immediate color change from pink to yellow was observed which is indicative of the loss of the dithioester end groups. The reaction mixture was then added dropwise to 10-fold excess of methanol, and the polymer was collected by centrifugation or by filtration. This process was repeated 3–5 times to obtain the pure α,ω -dithiol telechelics.

Characterization. NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for ¹H NMR and 75 MHz for ¹³C NMR. FT-IR spectra were obtained on a Digilab FTS 7000 equipped with a HgCdTe detector at wavenumbers from 4000 to 600 cm⁻¹. Gel permeation chromatography was carried out with a Viscotek 270 with a triple detector array (RALS, IV, RI, or UV) equipped with 2 GM-HHR-M and 1 GMHHR-L mixed bed Viscotek columns with THF as eluent at a flow rate of 1 mL min⁻¹. A Viscotek VE 1122 GPC solvent pump, a Viscotek VE 7510 GPC degasser, and Viscotek TriSEC software were also used. The thermal properties of the polymers and copolymers were measured by thermogravimetric analyses (TGA). The samples were heated to 700 °C at a heating rate of 5 °C/min under a dry nitrogen atmosphere in a TA Instruments 2950 thermogravimetric analyzer.

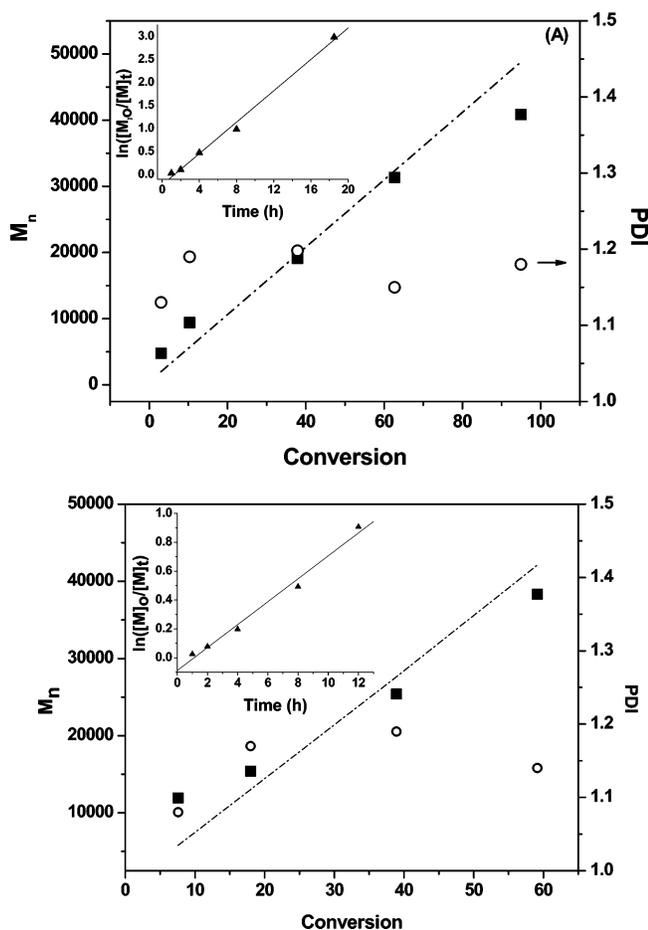


Figure 1. Evolution of molecular weight and PDI with conversion for polymerization of (A) LMA/CTA1 (B) MMA/CTA1. (■) $M_{n,GPC}$; (---) $M_{n,theory}$; (○) PDI. The inset shows the kinetic plot for polymerization of (A) LMA and (B) MMA at 60 °C (▲).

Results and Discussion

Lauryl methacrylate (LMA) and methyl methacrylate (MMA) were polymerized in benzene in the presence of AIBN as the free radical initiator and 1,4-bis(2-(thiobenzoylthio)prop-2-yl)benzene (CTA-1) as the CTA at 60 °C. To our knowledge, this represents the first example of RAFT polymerization for LMA. The initiator:CTA molar ratio was maintained at 1:1.6. The monomer:CTA was such that a theoretical molecular weight of 51 350 g/mol was expected at 100% conversion. Under these conditions, the ability of the difunctional CTA 1 to control the molecular weight and give narrow polydispersity for LMA is evident as shown by the linear increase of M_n with conversion and a low PDI (<1.2) throughout the course of the reaction (Figure 1A). Table 1 shows a summary of the molecular weights, polydispersities, and percent conversions for the polymerization. Figure 1A (inset) shows the kinetic plot for the polymerization of LMA and illustrates first-order kinetics as expected for a well-controlled radical polymerization. Similarly, the polymerization of MMA in the presence of CTA-1 showed the characteristics of a controlled radical polymerization with the observation of a linear increase of M_n with conversion and the maintenance of a low PDI over the course of the reaction (Figure 1B). The experimentally observed values of M_n deviated only slightly from the values predicted theoretically. First-order kinetics was obtained in the po-

Table 1. Summary of the RAFT Polymerizations of LMA, MMA, and Styrene

monomer	time (h)	conv (%) ^a	$M_{n,theory}$ ^b	$M_{n,GPC}$	PDI
lauryl MA	1	3.00	2 000	4 799	1.13
	2	10.3	5 707	9 429	1.19
	4	37.9	19 741	19 142	1.20
	8	62.7	32 359	31 333	1.15
	18.5	94.9	48 779	40 839	1.18
MMA	2	7.59	5 796	11 911	1.08
	4	18.0	13 027	15 415	1.17
	8	38.9	27 640	25 388	1.19
	12	59.1	42 110	38 333	1.14
styrene	4	1.72	3 655	3 889	1.15
	6	2.82	5 731	5 759	1.13
	12	6.81	13 178	11 699	1.14
	21	11.74	22 565	20 658	1.15
	28	15.74	29 917	24 560	1.20

^a Conversion was determined by NMR. ^b $M_{n,theory} = [M]_0/[CTA] \cdot MW_M \cdot conversion$.

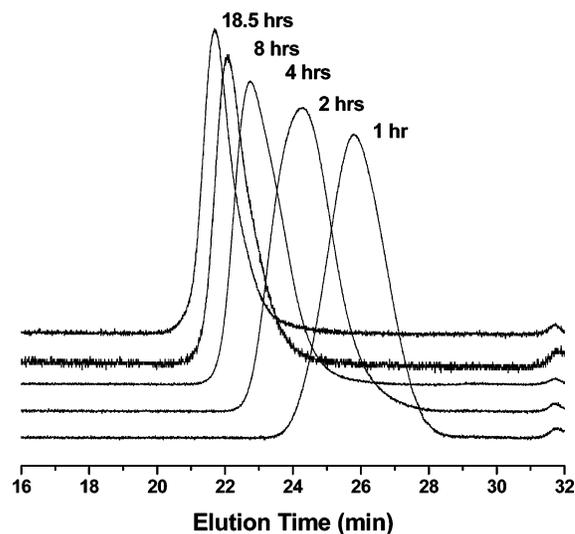


Figure 2. Size exclusion chromatograms for PLMA synthesized in the presence of CTA-1 in benzene at 60 °C.

lymerization of MMA as shown in Figure 1B (inset). Further evidence for a controlled radical polymerization can be seen in Figure 2, which shows an example of the stepwise evolution of MW for PLMA as determined by gel permeation chromatography. Close observation of the GPC traces reveal a slight low MW tail with increasing reaction time which is also reflected by a slight increase in the PDI (see Table 1). Styrene was polymerized under similar conditions using CTA-2 and yielded characteristics of a controlled radical polymerization. A summary for the polymerization of LMA, MMA, and styrene is also given in Table 1; however, for purposes of brevity, the actual kinetic data for the styrene polymerization are not shown (see Supporting Information for details of styrene polymerization).

As a result of the widely accepted mechanism for RAFT-mediated polymerization, the polymers obtained by employing a difunctional CTA of the structure presented here yield macromolecules containing a dithioester at both termini of a given chain. Chong and co-workers exploited this fact and illustrated the viability of difunctional CTAs where chain extension of a difunctional polymeric dithioester compound resulted in the formation of ABA triblock polymer architectures.¹⁵ While a small fraction of the polymer chains are initiated by a radical derived from AIBN, the majority of the chain ends bear the dithioester functionality

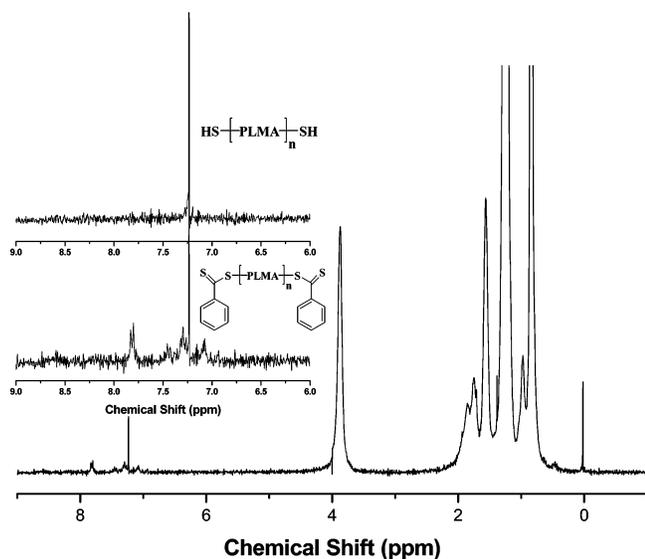


Figure 3. ^1H NMR spectra of PLMA prepared by RAFT-mediated polymerization before (inset lower) and after (inset upper) reaction with propylamine.

assuming an efficient reinitiation from the leaving group of the RAFT agent. The dithioester end-capped polymer has been shown to be the major product by multiple studies in which matrix-assisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectrometry¹⁶ and electrospray ionization mass spectrometry (ESI-MS)¹⁷ were employed for end-group analysis of RAFT-mediated polymers. Upon cleavage of the two dithioester groups at the chain ends, one is left with thiol functionalities as chain termini. Accordingly, the reaction between dithioesters and primary amines is well-known to occur rapidly at ambient temperatures leading irreversibly to thioamides and thiols.¹⁸ While aminolysis of dithioester-containing RAFT polymers is not new, until now, the technique has mostly been used as a probe for structural analysis and confirmation, i.e., chain branching and block formation.¹⁹ In addition, Lima et al. used aminolysis to access a heterofunctional telechelic as an intermediate for the synthesis of α,ω -dihydroxy telechelic polymethacrylates via Michael addition of hydroxyethyl acrylate.^{3a} As far as we know, there are no accounts in the literature which describe the use of aminolysis and difunctional CTAs to directly access α,ω -dithiol telechelics. In the current work, polymers synthesized using difunctional chain transfer agents were subjected to aminolysis by reaction of the dithioester termini with propylamine (see Scheme 2). The addition of propylamine to a solution of the dithioester end-capped polymers was accompanied by a rapid color change from pink to yellow, indicating the aminolysis of the RAFT end group. After purification, the extent of the reaction was monitored by ^1H NMR. As shown in Figure 3, the aromatic protons of the dithioester end groups could not be observed after the reaction with propylamine within the sensitivity of the NMR method. It should be noted that in the present case NMR alone cannot be used to suggest the quantitative reduction of the dithioester end group since the signal attributed to the aromatic end group is extremely low. Thus, in addition to NMR, UV-vis spectroscopy was also used as a simple procedure for the characterization of the resulting polymers. The dithioester moiety has a strong absorption band at 302 nm which allows one to use UV-vis spectroscopy as a simple procedure

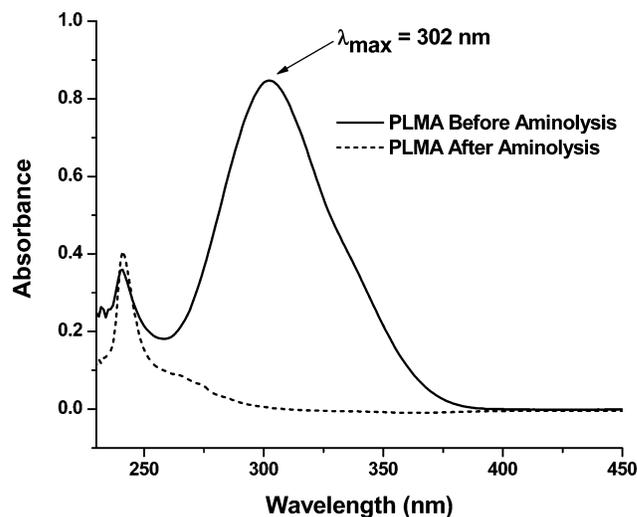


Figure 4. UV-vis absorption spectra of PLMA synthesized by RAFT-mediated polymerization before (—) and after (---) reaction with propylamine.

for the characterization of the resulting polymers (Figure 4). As a result of aminolysis, the absorption due to the dithioester is absent, indicating, along with the NMR result, a near-quantitative reduction of the dithioester termini to yield α,ω -dithiol telechelics. In contrast to the highly colored (pink) polymers prior to aminolysis, the final product was observed as pristine white in the case of PMMA and PS and colorless in the case of PLMA.

To avoid the oxidative coupling of the thiol end groups, a similar procedure to that used by Lima et al. was adopted for the current work.³ Despite taking all precautions, such as degassing the reaction mixture, oxidative coupling of the thiol termini can still occur upon treatment with a primary alkylamine. Lima et al. showed that by addition of a small amount of antioxidant in the form of aqueous sodium bisulfite ($\text{Na}_2\text{S}_2\text{O}_4$) the formation of disulfides which result from oxidative coupling of thiols could be effectively suppressed. The presence or absence of the disulfide species can easily be observed by gel permeation chromatography in which such species would appear at an elution volume corresponding to a MW twice that of the original monofunctional thiol end-capped polymer. For the difunctional polymers presented here, the MW of the disulfide species could be larger than 2 times due to the multifunctionality. However, under the conditions described above (addition of $\text{Na}_2\text{S}_2\text{O}_4$), the presence of the oxidative coupling products was not observed as shown by the GPC traces for a poly(lauryl methacrylate) sample in Figure 5. Furthermore, no significant change was observed in the polydispersity of the pLMA before (PDI 1.15, M_n 48 125) and after (PDI 1.17, M_n 47 446) aminolysis. A small decrease in the MW was observed after aminolysis, which is consistent with the reduction of the dithioester termini to thiol functional groups. The exact value of the change in MW is difficult to resolve by GPC since the change is relatively small in contrast to the total MW of the polymer. Alternatively, in the absence of sodium sulfite in the aminolysis procedure, we explored other procedures for the reduction of the disulfide products such as Zn/acetic acid (50 °C) in a subsequent step following aminolysis.²⁰ This reductive system showed no advantages over the previously described procedure in which sodium sulfite was employed.

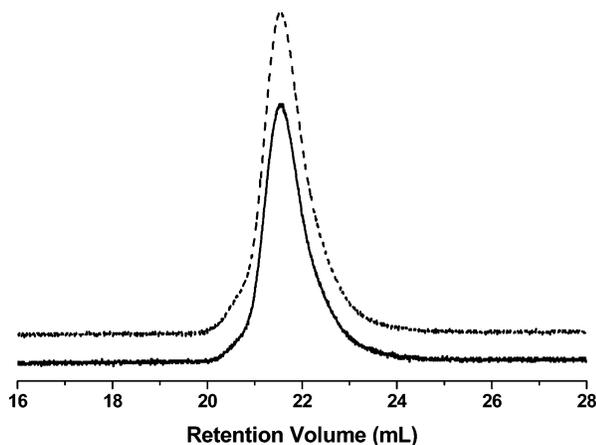


Figure 5. GPC chromatograms of PLMA before (—) and after (---) aminolysis with propylamine in the presence of $\text{Na}_2\text{S}_2\text{O}_4$. The results show no evidence for the formation of disulfides.

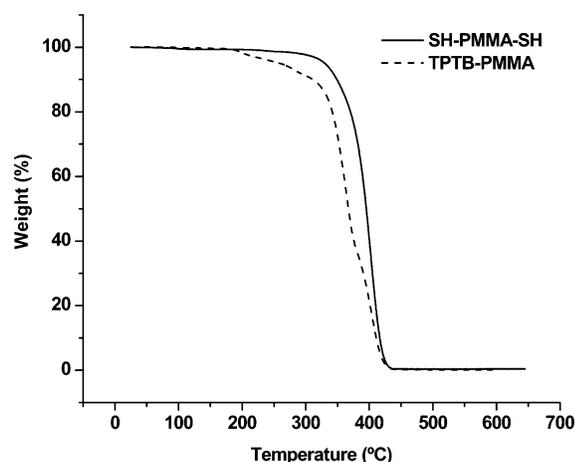


Figure 6. TGA traces of PMMA as synthesized by RAFT (---) and the α,ω -thiol telechelic PMMA (—) obtained after aminolysis.

The thermal stability of the α,ω -thiol telechelics was determined by thermogravimetric analysis under nitrogen. Figure 6 shows a typical example of the thermal properties observed for PMMA dithiol telechelics ($M_n = 14\text{K}$). The lowered thermal stability (onset of weight loss $\sim 200^\circ\text{C}$) of the polymers synthesized by RAFT can be attributed to the presence of the labile dithioester moiety at the chain end. It should be noted that the onset of thermal degradation should vary with molecular weight since chain ends play a more important role at lower molecular weights. However, once the dithioester end groups are replaced by thiol functionalities at the chain end, the onset of weight loss is first observed at $\sim 300^\circ\text{C}$. Along with a loss of color in the polymer, the absence of the dithioester functionality imparts greater thermal stability in the α,ω -thiol telechelics.

Adsorption studies of the α,ω -thiol telechelics onto gold surfaces are currently underway in our lab with the goal of defining parameters necessary for the formation of multiply bound polymer chains (MBPCs). The thiol functional group was chosen as a model system due in part to the vast amount of literature available for gold–thiolate interaction.²¹ Adsorption kinetics and geometric parameters are being obtained by surface plasmon resonance (SPR) spectroscopy and quartz crystal microbalance (QCM), respectively. Some preliminary QCM results for the adsorption of α,ω -thiol telechelic polystyrene onto gold are shown in the Sup-

porting Information (Figure S3). Geometric parameters such as grafting density (σ , chains/ nm^2) and interchain spacing (R , $1/\sigma$) can be extracted from the QCM experiments and show a strong dependence on the MW of the adsorbed material. A more detailed account of the adsorption studies for the materials presented here will be addressed in a forthcoming publication.

Conclusions

A straightforward procedure to α,ω -dithiol telechelics has been developed on the basis of reversible addition fragmentation chain transfer (RAFT) polymerization. The technique allows α,ω -thiol functionalized polymers to be prepared directly from a difunctional chain transfer agent with only one postpolymerization reaction. The dithioester termini were converted to thiols by way of aminolysis in the presence of an antioxidant to yield the difunctional polymers with narrow molecular weight distributions. The α,ω -thiol telechelics showed greatly improved thermal properties in the absence of the dithioester end group. The present method offers the advantages of mild reaction conditions associated with RAFT polymerization and applicability to a wide range of monomer functionalities. The adsorption of the α,ω -dithiol telechelics on gold surfaces is currently under investigation with an interest in the formation of multiply bound polymer chain (MBPCs).

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Supporting Information Available: Details of styrene polymerization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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