Synthesis of Monocyclic and Linear Polystyrene Using the Reversible Coupling/Cleavage of Thiol/Disulfide Groups

Michael R. Whittaker,[†] Yong-Keng Goh,[†] Hesna Gemici,[‡] Thomas M. Legge,[‡] Sebastien Perrier,[‡] and Michael J. Monteiro*,[†]

Australian Institute of Bioengineering and Nanotechnology, School of Molecular and Microbial Sciences, University of Queensland, Brisbane QLD 4072, Australia, and Department of Colour and Polymer Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, U.K.

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ABSTRACT: By carefully controlling the concentration of α,*ω*-thiol polystyrene in solution, we achieved formation of unique monocyclic polystyrene chains (i.e., polymer chains with only one disulfide linkage). The presence of cyclic polystyrene was confirmed by its lower than expected molecular weight due to a lower hydrodynamic volume and loss of thiol groups as detected by using Ellman's reagent. The α,*ω*-thiol polystyrene was synthesized by polymerizing styrene in the presence of a difunctional RAFT agent and subsequent conversion of the dithioester end groups to thiols via the addition of hexylamine. Oxidation gave either monocyclic polymer chains (i.e., with only one disulfide linkage) or linear multiblock polymers with many disulfide linkages depending on the concentration of polymer used with greater chance of cyclization in more dilute solutions. At high polymer concentrations, linear multiblock polymers were formed. To control the MWD of these linear multiblocks, monofunctional X−PSTY (X = $PhCH_2C(=S)-S-$) was added. It was found that the greatest ratio of X−PSTY to X−PSTY−X resulted in a low M_n and PDI. We have shown that we can control both the structure and MWD using this chemistry, but more importantly such disulfide linkages can be readily reduced back to the starting polystyrene with thiol end groups, which has potential use for a recyclable polymer material.

Introduction

Lowig[1] showed that polymers containing disulfide linkages provided remarkable properties: they were flexible at low temperatures and showed high resistance to organic compounds, ozone, and weathering.[2] The ease of disulfide exchange with thiols provides a facile route to functionalized linear polymers or gels with important thiol-containing compounds such as biomolecules (e.g., antisense oligonucleotides).[3] Other methods of reduction of disulfide bonds to thiols include dithiolthreitol[4,5] and zinc dust.[6] This makes polymers with such linkages attractive for applications in biomedical devices, coatings, drug delivery, and recyclable materials.

Tsarevsky and Matyjaszewski[7] showed that by atom transfer radical polymerization (ATRP), a "living" radical polymerization technique that allows the production of near uniform polymer chains with functional end groups, α,*ω*-telechelic polystyrene with Br groups could be made. Through some nontrivial chemistry, they were able to synthesize telechelic polystyrene with thiol end groups and showed that disulfide linkages between the polymer chains could be formed using $FeCl_3$ as the oxidant. The molecular weight analysis showed a bimodal distribution, in which they assigned the first low molecular weight peak to unreacted α,*ω*-thiol polystyrene and the second broad peak at higher molecular weight to the oxidized polymer containing disulfide linkages. They further showed that this was a reversible system and these polymer chains could be reduced back to the starting polymer.

Lima et al.[8] showed that telechelic polymers where one chain end consisted of a thiol and the other of an alcohol could be readily synthesized using the reversible addition−fragmentation chain transfer (RAFT) polymerization technique. The RAFT moiety ($S{=}C(Ph)S-$) on the chain end undergoes a facile aminolysis[9] to form the corresponding thiol. Patton et al.[10] then showed that α,*ω*-thiol polystyrene could be prepared via a facile route of using a difunctional RAFT agent, in which the resulting polymer was reacted with amine to give the thiol end groups (dimercapto-terminated polystyrene). The activating Z group used by Patton et al.[10] was a phenyl moiety that has been found to severely retard the rate of polymerization and produce 3- and 4-arm stars.[11−14] In this work we used the benzyl (CH_2PH) Z group to avoid these deleterious effects due to the faster fragmentation rate.[15]

The aim of this work was to control the structure (cyclic or linear multiblock polymers) and molecular weight distribution (see Scheme 1). The α,*ω*-telechelic polystyrene (with thiol end group) was synthesized using a difunctional RAFT agent (chain transfer agent (CTA)) with a benzyl (CH_2Ph) activating group. The $S{=}C(CH_2Ph)S-$ difunctional polystyrene chains were converted to the α,*ω*-thiol polystyrene by aminolysis in dilute solutions. The synthesis and control of molecular weight of linear multiblock polymers was carried out through the oxidation of the α,*ω*-thiol polystyrene in the presence of varying amounts of monofunctional thiol polystyrene (prepared using a monofunctional RAFT agent, 1-phenylethyl phenyldithioacetate (PEPDTA).

Experimental Section

Chemicals. Styrene (STY, 99% pure, Aldrich) was passed through a column of basic alumina to remove inhibitor immediately prior to use. 2,2-Azobis(isobutyronitrile) (AIBN, 98% pure, Fluka) was recrystallized twice from methanol prior to use. 1,3-Diissopropenylbenzene (Aldrich, 97%), tetrahydrofuran (THF, HPLC grade, LAB-SCAN, 99.8%), toluene (HPLC grade, LAB-SCAN, 99.8%), *n*-hexane (AR grade, UNIVAR), anhydrous methanol (MeOH, 99.9% pure, Mallinckrodt), chloroform (99% pure, LAB-

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[†] University of Queensland.
[‡] University of Leeds.
* To whom correspondence should be addressed: e-mail m.monteiro@uq.edu.au.

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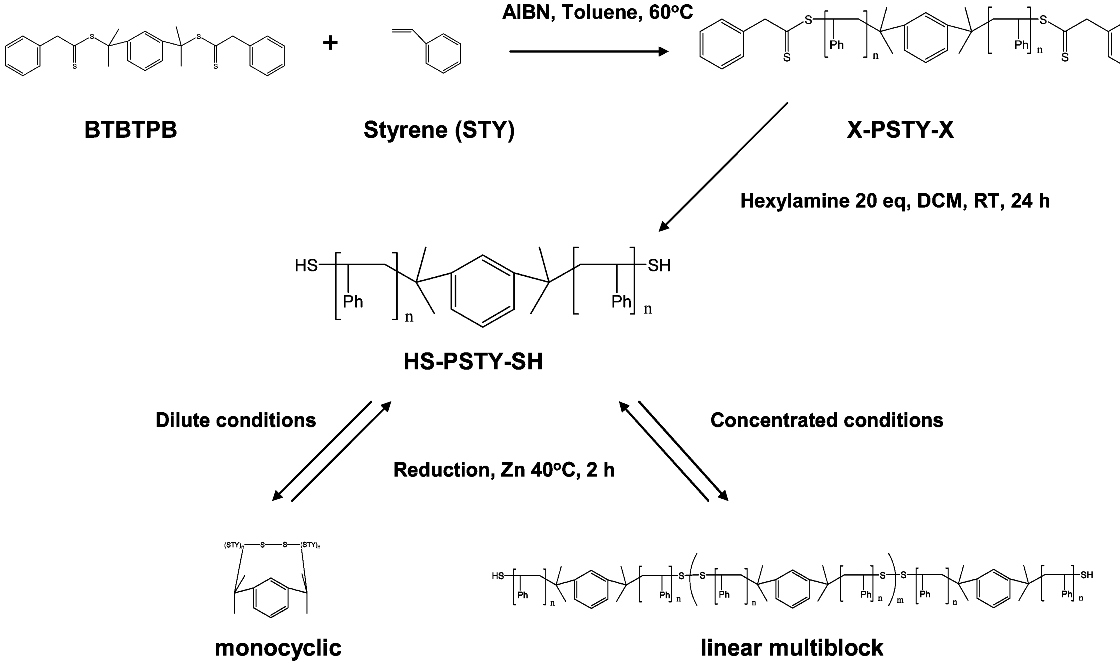
Scheme 1. Synthesis of Monocyclic (One Disulfide Linkage) and Linear Multiblock Polymers through Thiol−Thiol Coupling Reactions[a]



[a] The formed polymers can easily be reduced back to the starting polymer (HS−PSTY−SH), a reversible system.

SCAN), dichloromethane (DCM, 99% pure, Aldrich), hexylamine (99% pure, Aldrich), iron(III) chloride ($FeCl_3$, BDH, 98% pure), dimethylformamide (DMF, 99% Aldrich), glacial acetic acid (LAB-SCAN, 99%), zinc dust (Lancaster, 99%), and alumina oxide 90 active neutral (Merck) were obtained at the highest purity and used without further purification unless otherwise stated. Phenyldithioacetic acid (PDA)[16] and 1-phenylethyl phenyldithioacetate (PEPDTA)[17] were prepared according to literature procedures.

Synthesis of 1,3-Bis(2-(thiobenzylthio)prop-2-yl)benzene (BTBTPB).[16] 1,3-Bis(2-thiobenzylthio)prop-2-yl)benzene (BTPTPB) was prepared via the following method. Phenyldithioacetic acid (PDA) (8.7 g, 51.7 mmol) was combined with 1,3-diisopropenylbenzene (3.67 g, 23.2 mmol) in the presence of a small amount of an acid catalyst (toluene-*p*-sulfonic acid) in carbon tetrachloride (100 mL). The mixture was then refluxed in an oil bath at 65 °C for 63 h. The mixture was concentrated via rotary evaporation and purified through a column of alumina oxide (using a mixture of 95% of *n*-hexane and 5% of diethyl ether as an eluent). An orange oil product was collected after solvent removal. The purity of the compound was verified by NMR, and elemental analysis and was better than 99%. ^{1}H NMR ($CDCl_3$): $\delta = 1.8$ s (12H), $\delta = 4.2$ s (4H), $\delta = 7.3$ m (13H), $\delta = 7.5$ s (1H). ^{13}C NMR ($CDCl_3$): 28.1, 56.3, 59.2, 124.8, 127.1, 128.9, 137.2, 142.8, and 238.2.

Synthesis of Monofunctional Polystyrene ($PhCH_2C(=S)-S-$PSTY, or X−PSTY). In a typical polymerization experiment, STY (18.14 g, 8.66 M), AIBN (14.79 mg, 4.48×10^{-3} M), and PEPDTA (114.73 mg, 2.09×10^{-2} M) were charged to a 20 mL ampule. The polymerization mixture was deoxygenated by four successive freeze−pump−thaw cycles, sealed, placed in an oil bath, and polymerized at 60 °C for 8 h, after which time it was quenched in liquid nitrogen. The polymer was precipitated in MeOH, filtered, and dried under high vacuum at 25 °C for 24 h to give a yellow powder. The molecular weight distribution of the polymer was measured by size exclusion chromatography (SEC) ($M_n = 6169$ and PDI = 1.09).

Synthesis of α,*ω*-Telechelic Polystyrene ($PhCH_2C(=S)-S-$PSTY$-S-C(=S)CH_2Ph$, or X−PSTY−X).[18] In a typical polymerization experiment, STY (29.0 g, 5.56 M), AIBN (20.6 mg, 2.50×10^{-3} M), and BTBTPB (617.0 mg, 2.49×10^{-3} M) were dissolved in toluene (17.9×10^{-3} L). The polymerization mixture was degassed by four successive freeze−pump−thaw cycles, sealed, and polymerized at 60 °C for 20 h. The polymerization mixture was quenched in liquid nitrogen, diluted with THF, and exposed to air. The polymer was then precipitated in MeOH, filtered, and dried under high vacuum at 25 °C for 24 h to yield a yellow powder. The molecular weight distribution was measured by size exclusion chromatography (SEC), giving an $M_n = 3679$ and PDI = 1.11.

Conversion of Dithioesters to Thiol End Groups.[8] **Aminolysis of $PhCH_2C(=S)-S-$PSTY (X−PSTY) to HS−PSTY.** In a typical aminolysis experiment, a solution of hexylamine (0.656 g, 0.858 mL, 6.48 mmol, 648 mM) in THF was added to a solution of PSTY (2 g, $M_n = 6169$, 0.32 mmol, 32.4 mM) in THF. The reaction mixture was allowed to stir over night at room temperature. The thiolated polymer was precipitated into methanol, filtered, washed with water and methanol, and dried under vacuum at 25 °C. Conversion of the end groups to thiols was determined by UV−vis spectroscopy.

Aminolysis of $PhCH_2C(=S)-S-$PSTY$-S-C(=S)CH_2Ph$ (X−PSTY−X) to HS−PSTY−SH. In a typical aminolysis experiment, hexylamine (1.06 mL, 1 M, 10 equiv) was added to a solution of $PhCH_2C(=S)-S-$PSTY$-S-C(=)CH_2Ph$ (0.370 g, 2.5×10^{-2} M, 1 equiv) in 3 mL of DCM. In all experiments, a 20-fold excess of hexylamine to thiol end groups was maintained. The reaction mixture was stirred overnight at room temperature, and then the polymer precipitated into methanol, filtered, and dried under high vacuum at 25 °C for 24 h to give a white powder. The molecular weight distribution was measured by size exclusion chromatography (SEC).

Aminolysis of $PhCH_2C(=S)-S-$PSTY$-S-C(=S)CH_2Ph$ via Slow Addition Methodology. A solution of $PhCH_2C(=S)-S-$PSTY$-S-C(=S)CH_2Ph$ (0.075 g, 2.5×10^{-4} M) in 10 mL of DCM was added via a syringe pump (overnight) to a stirred solution of hexylamine (1.06 mL, 0.1 M) in 69 mL of DCM. After aminolysis, the volume of the mixture was reduced to ~20 mL using a nitrogen flow, and the polymer precipitated into a large volume of methanol. The polymer was filtered and dried under high vacuum at 25 °C for 24 h to give a white powder. The molecular weight distribution was measured by size exclusion chromatography (SEC).

Aminolysis of a Mixture of X−PSTY−X and X−PSTY. Three ratios (35, 5, and 1) of X−PSTY−X to X−PSTY were aminolyzed in the presence of 20-fold excess of hexylamine to thiol end groups. In a typical aminolysis experiment, X−PSTY (0.308 g, 8.33×10^{-5} mol) and X−PSTY−X ($M_n = 4450$ and PDI = 1.09, 0.074 g, 1.67×10^{-5} mol) were dissolved into 3.5 mL of DCM. To this stirred solution was added hexylamine (0.48 mL, 4.89×10^{-3} mol). The reaction mixture was stirred overnight at room temperature, and

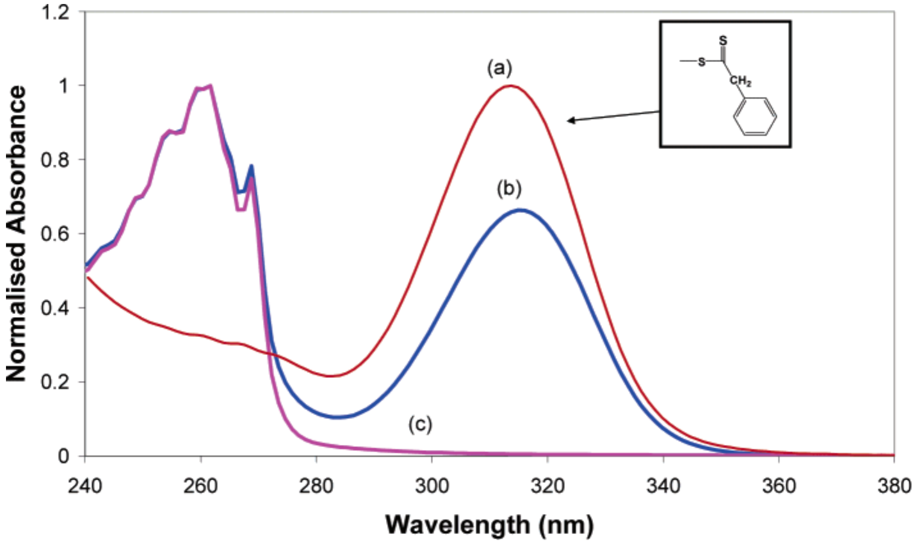


Figure 1. Typical UV/vis spectra of (a) difunctional RAFT agent, BTBTPB, (b) X−PSTY−X, and (c) X−PSTY−X hydrolyzed with hexylamine at room temperature in THF (where X = $-SC(CH_2Ph){=}S$).

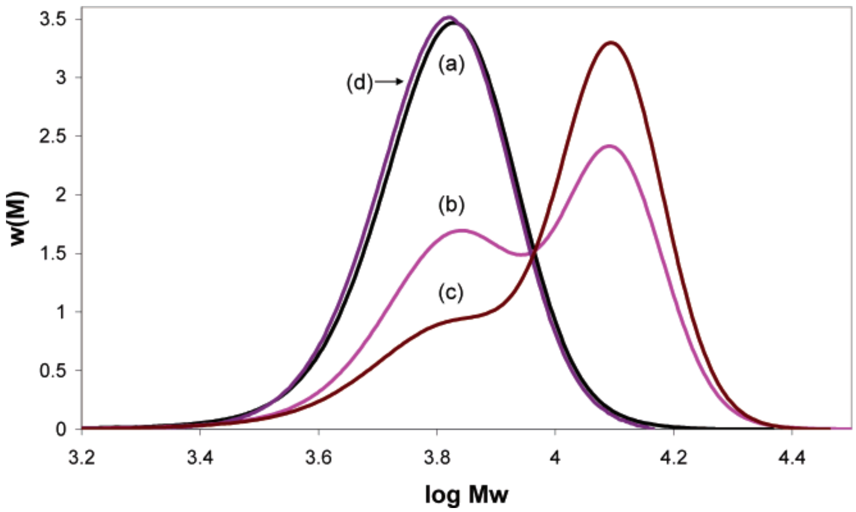


Figure 2. SEC chromatograms (normalized weight distribution) of (a) monofunctional X−PSTY (M_n = 6169, PDI = 1.09), (b) aminolysis of 2.48 × 10^{-2} M of PSTY−X with 2.57 M hexylamine in DCM for 12 h, (c) oxidized polymer with Fe(III)Cl_3 (0.0769 M) in THF for 72 h, and (d) reduced with zinc and acetic acid.

the polymer precipitated using a large volume of methanol. The polymer was filtered and dried under high vacuum at 25 °C for 24 h to give a white powder. The molecular weight distribution was measured by size exclusion chromatography (SEC).

Oxidation of Thiol-Terminated Polymer. In a typical oxidation experiment, $FeCl_3$ (0.108 g, 6.7 × 10^{-4} mol) was added to a solution of X−PSTY−X (2.5 × 10^{-3} M, 0.100 g, 2.70 × 10^{-5} mol) in DMF (1 mL). The reaction mixture was stirred at 60 °C. Samples were withdrawn periodically, diluted with THF, and analyzed by SEC. The oxidized polymer was precipitated in a large volume of methanol, filtered, and dried in a high vacuum oven overnight at 25 °C. The final molecular weight distribution was measured by size exclusion chromatography. The polymer concentrations used in these experiments were equal to those used in the aminolysis experiments.

Reduction of Oxidized Polymers. In a typical reduction experiment, a solution of acetic acid (1 mL) and zinc powder (100 mg) was added to a solution of X−PSTY−X (50 mg) in THF (2 mL). The mixture was stirred at 40 °C for 4 h. The mixture was then passed through basic aluminum oxide, precipitated in methanol, filtered, and dried in a high vacuum oven overnight at 25 °C. The resulting polymer was analyzed by SEC.

Size Exclusion Chromatography. Size exclusion chromatography (SEC) measurements were performed using a Waters Alliance 2690 separations module equipped with an autosampler, column heater, differential refractive index detector, and a photodiode array (PDA) connected in series. For polystyrene analysis, HPLC grade tetrahydrofuran was used as eluent at a flow rate of 1 mL min^{-1}. The columns consisted of three 7.8 × 300 mm Waters Styragel GPC columns connected in series, comprising two linear Ultrastyragel and one Styragel HR3 column. Polystyrene standards ranging from 2 000 000 to 517 g mol^{-1} were used for calibration.

UV/Vis Spectroscopy. UV spectra were recorded on a Perkin-Elmer Lambda2 UV−vis spectrometer in the wavelength range from 220 to 500 nm. Measurements were carried out in solution (THF).

Nuclear Magnetic Resonance (NMR). NMR spectroscopy was carried out using a Bruker Avance DRX 500 spectrometer operating at 500.13 MHz for protons and equipped with a 5 mm triple resonance *z*-gradient probe.

Results and Discussion

The RAFT process was used to prepare α,*ω*-telechelic polystyrene with $S{=}C(CH_2Ph)S-$ on both chain ends (X−PSTY−X)[18] or on one chain end (X−PSTY). To determine whether chain-end aminolysis quantitatively converted all X groups to thiols, we carried out UV−vis analysis before and after polymer treatment with hexylamine. Figure 1 shows typical

Table 1. Molecular Weight Data for the Reaction of Difunctional X−PSTY−X (Where X = −SC(CH$_2$Ph)═S, M_n = 3679, PDI = 1.11) in the Presence of Hexylamine (20-Fold Excess to Thiol End Groups) for 12 h in THF at Room Temperature under Dilute Conditions[a]

		aminolysis (12 h)		[Ox] (24 h)		[Ox] (72 h)		reduced after Ox	
expt	[X−PSTY−X] (mol L^{-1})	M_n	PDI	M_n	PDI	M_n	PDI	M_n	PDI
1	2.5×10^{-2}	7023	1.87	6425	2.43	14516	2.81	3564	1.11
2	2.5×10^{-3}	3692	1.14	5248	2.56	5868	2.39	3428	1.15
3	2.5×10^{-4}	4204	1.27	3796	1.69	4082	1.66	3637	1.09
4[b]	2.5×10^{-4}	3154	1.20						

[a] This polymer was then precipitated and filtered and oxidized with Fe(III)Cl$_3$ (7.7×10^{-2} M) for 24 and 72 h in THF at 60 °C and reduced with zinc dust and acetic acid. [b] X−PSTY−X in THF was fed via a syringe pump over a 3 day period in a solution of hexylamine and THF.

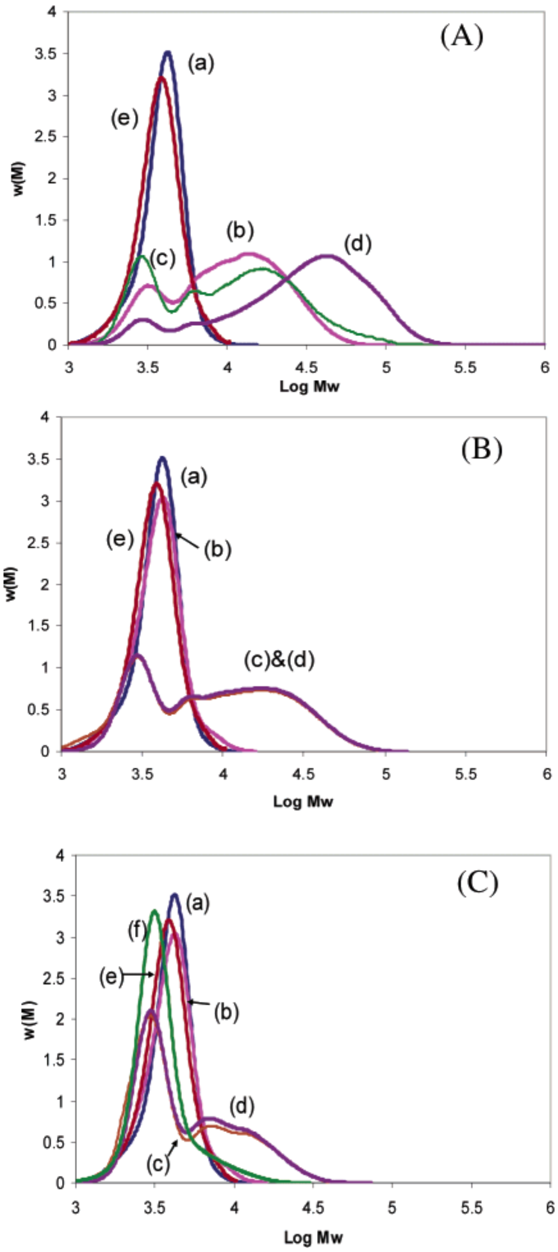


Figure 3. SEC chromatograms (normalized weight distribution) after aminolysis, oxidation, and reduction at three different starting X−PSTY−X concentrations (A) 2.49×10^{-2} M, (B) 2.48×10^{-3} M, and (C) 2.44×10^{-4} M (refer to Table 1 for full details): curves (a) X−PSTY−X (M_n = 3679, PDI = 1.11), (b) after 12 h aminolysis, (c) after 24 h oxidation, (d) after 72 h oxidation, (e) reduction with zinc, and (f) slow addition of X−PSTY−X to hexylamine solution (3 days, final X−PSTY−X concentration equals 2.5×10^{-4} M).

UV−vis spectra of the chain transfer agent (CTA, BTBTPB, curve a), S═C(CH$_2$Ph)S−PSTY−S(CH$_2$Ph)C═S (X−PSTY−X, curve b), and X−PSTY−X after aminolysis (curve c). The CTA and X−PSTY−X have a strong absorbance between 270 and 350 nm, with a maximum close to 318 nm corresponding to the S═C(CH$_2$Ph)S− group. After aminolysis of X−PSTY−X the peak between 270 and 350 nm disappears, showing that all end groups are converted to thiols.

A monofunctional polySTY (X−PSTY) was used as a model compound to determine the extent of oxidation of thiols to disulfides and whether oxidation occurred during aminolysis. Oxidation of X−PSTY should result in a PSTY−S−S−PSTY polymer with double the molecular weight of X−PSTY. Figure 2 shows the molecular weight distributions (MWDs) before (curve a) and after (curve b) aminolysis carried out for 12 h using a 20-fold excess of hexylamine to thiol end groups, after further oxidation with a strong oxidizing agent, Fe(III)Cl$_3$, for 72 h (curve c), and then after reduction with zinc (curve d). All SEC chromatograms are normalized to weight and can be used for direct quantification of the degree of oxidation. After aminolysis a peak at twice the molecular weight of the initial polymer appeared, representing ~56% of the total polymer. This peak increased in size after 72 h oxidation with FeCl$_3$, representing ~80% of total polymer. However, there remained a small amount of polymer in the low molecular weight peak, which could be attributed to unoxidized thiol chain ends, conversion of free thiols or disulfides to alternative products formed during oxidation, and/or the presence of dead polymer that forms during the RAFT polymerization. Reduction of the disulfide linkages with zinc powder resulted in a MWD that overlapped with the starting polymer (X−PSTY), showing that all disulfide linkages were converted back to thiols (curve d).

Synthesis of Monocyclic PSTY. Cyclic polymers have different hydrodynamic[19,20] and thermal properties[21] as compared to their linear counterparts of the same chain length. Most cyclic polymers have been synthesized using anionic polymerization to make telechelic polymers that can be further coupled in a dilute solution.[22−24] There have been no reports of polystyrene cyclic polymers that can be reversibly converted back to the linear α,ω-telechelic polymer.

The synthesis of monocyclic polymers (with only one disulfide linkage) using X−PSTY−X was carried out by first converting the dithioesters to thiols and then oxidizing them under dilute conditions. The MWDs after aminolysis and oxidation of X−PSTY−X (M_n = 3679, PDI = 1.11) at three different polymer concentrations are given in Figure 3. It should be noted that all SEC chromatograms were normalized to weight and thus could be used for the quantitative determination of monocyclic polymer. At the highest X−PSTY−X concentration of 2.49×10^{-2} M (Figure 3A), MWD is multimodal after aminolysis (curve b). There is a low molecular weight peak (maximum at 2722) that is even lower than the starting polymer MWD (curve a), attributed to the formation of a cyclic polymer with a reduced hydrodynamic volume. This peak remained even after extensive oxidation for 24 and 72 h (curves c and d, respectively). Reduction of the polymer (oxidized after 72 h) gives a MWD that overlays that of the starting polymer. The lower molecular weight peak, assigned to monocyclic polySTY,

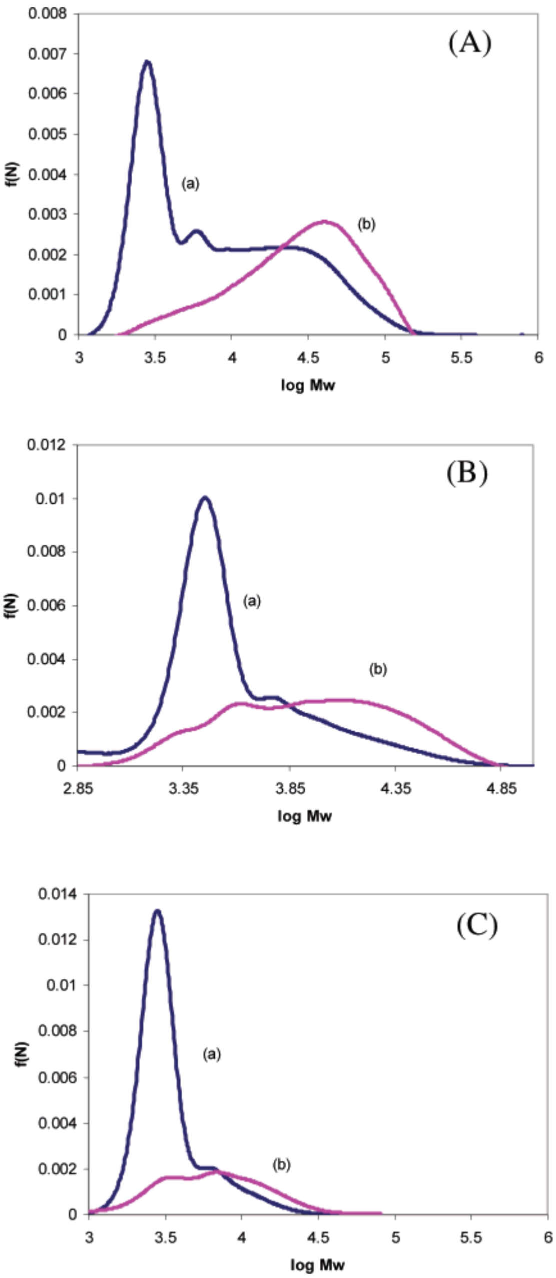


Figure 4. SEC chromatograms (normalized number distribution) after 72 h oxidation at three different starting X−PSTY−X concentrations of (A) 2.49 × 10^{-2} M, (B) 2.48 × 10^{-3} M, and (C) 2.44 × 10^{-4} M: curves (a) RI detection; (b) UV−vis detection at 324 nm.

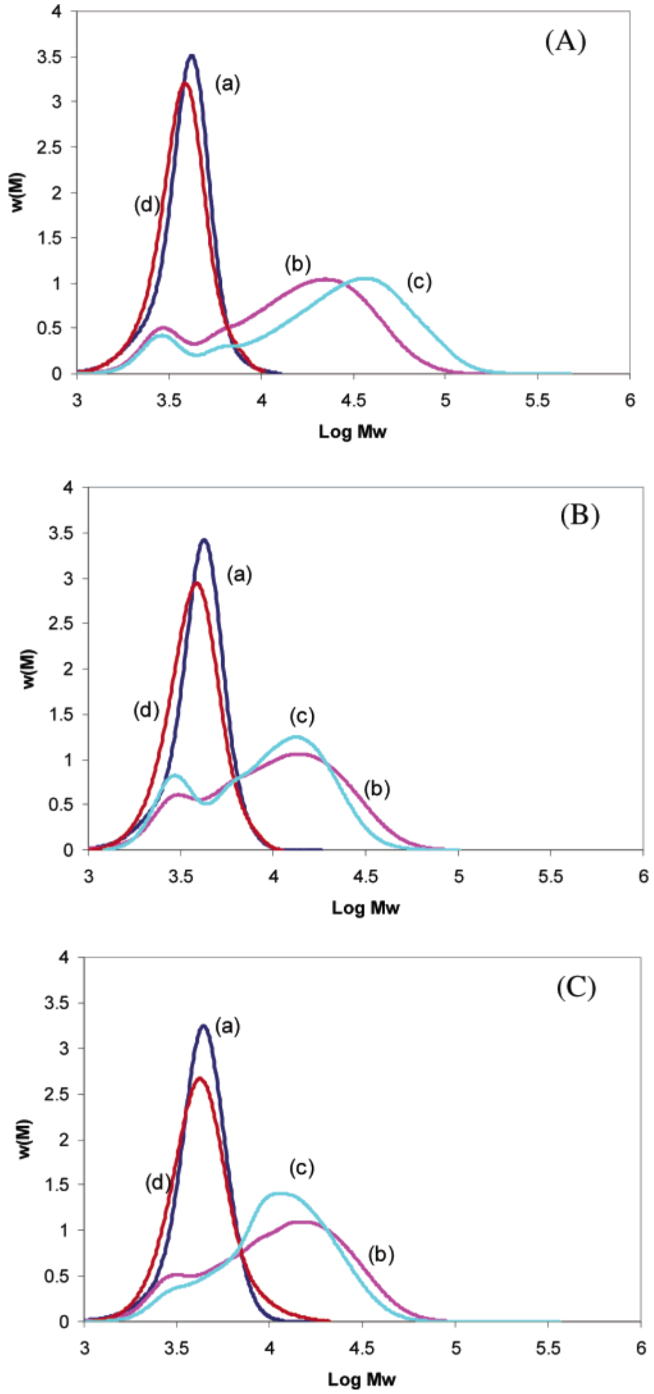


Figure 5. SEC chromatograms (normalized weight distribution) for the aminolysis, oxidation, and reduction of varying ratios of starting X−PSTY−X to X−PSTY: (A) 35:1, (B) 5:1, and (C) 1:1. Curves (a) starting polymers, (b) aminolysis with 20-fold hexylamine to thiol end groups, (c) oxidation after 48 h, and (d) reduction with zinc and acetic acid (see Table 2 for details).

is ∼1000 lower than the peak maximum of the reduced polymer, a difference beyond SEC error. These results strongly support the formation of monocyclic polySTY and some higher molecular weight linear multiblock polySTY.

A decrease in the X−PSTY−X concentration by an order of magnitude (2.5 × 10^{-3} M, Figure 3B) showed that after aminolysis (curve b) there was little or no change in the MWD compared to the starting polymer. After oxidation (24 h, curve c), however, the MWD is multimodal, with a low molecular weight monocyclic polymer peak (close to 2700) and high molecular weight linear multiblock polymer chains. A greater oxidation time (72 h, curve d) did not change the MWD. At the lowest polymer concentration used (2.5 × 10^{-4} M, Figure 3C) there was little or no change in the MWD after aminolysis (curve b), but after 24 and 72 h of oxidation the monocyclic peak became substantially higher than in the reactions at higher concentrations (curves c and d). To increase the amount of cyclic polymer, we fed the polymer solution into a solution of hexylamine over a 3 day period using a syringe pump (Figure 3C, curve f). The increase in monocyclic polymer was also supported from the M_n and PDI data given in Table 1. The decreased concentration of polymer after 72 h oxidation resulted in a decrease in M_n from 14 516 (2.5 × 10^{-2} M) to 4082 (2.5 × 10^{-4} M) and PDI (from 2.81 to 1.66, respectively). The slow feed reaction produced the best result with an M_n of 3154 and PDI of 1.2, which were the lowest values found for all reactions.

At a concentration of 2.5 × 10^{-4} M the weight percent (determined from the weight distribution in the SEC trace) and

Table 2. Molecular Weight Data for the Reaction of Difunctional X−PSTY−X (Where X = −SC(CH$_2$Ph)═S, M_n = 3679, PDI = 1.11) and Monofunctional X−PSTY (M_n = 4540, PDI = 1.09) after Aminolysis with 20-Fold Excess of Hexylamine to Thiol End Groups in THF at Room Temperature[a]

		starting polymer		aminolysis		[Ox] (48 h)		reduction	
expt	[X−PSTY−X]/[X−PSTY][a]	M_n	PDI	M_n	PDI	M_n	PDI	M_n	PDI
5									
6	35	3685	1.12	8896	2.28	11630	2.83	3527	1.16
7	5	3751	1.12	6641	1.54	8465	1.75	3494	1.12
8	1	4017	1.11	7703	1.92	6435	1.59	3938	1.16

[a] The polymer was precipitated and oxidized with Fe(III)Cl$_3$ in DMF for 48 h at 60 °C and then reduced with zinc and acetic acid.

percent of monocyclic polySTY chains (determined from the number distribution in the SEC trace) were 27 and 55%, respectively, after 72 h oxidation. Under slow feed conditions the weight percent and percent of monocycles chains increased to 83% and 90%, respectively, after aminolysis. Although the data strongly supported the formation of monocyclic structures, convincing proof was found from the addition of the Ellman's reagent to the polymer after oxidation. In these experiments, the Ellman's reagent adds to all residual thiols, and thus the resulting chain ends will have an absorbance at 324 nm corresponding to the 2-nitrobenzoic acid moiety. Figure 4 showed the MWDs of the various polymers after 72 h oxidation using the refractive index and UV−vis (324 nm) detectors. In all the figures, it was clearly seen that the low molecular weight peak contained a very small amount of nitrobenzoate, supporting our argument that the low molecular weight peak is cyclic in structure.

However, the mechanism for thiol−thiol coupling is not straightforward and is complicated by other reactions, including the exchange reaction between thiols and disulfides. Our results suggest that thiol exchange with PSTY disulfides was not observed since the addition of a monofunctional HS−PSTY and with FeCl$_3$ did not result in a loss of the amount of cyclic polymer.

Effect of Coupling Reactions of HS−PSTY−SH and HS−PSTY on MWD. The monocyclic polymer was preferentially formed under very dilute conditions. Under more concentrated conditions (experiment 1, [X−PSTY−X] = 2.48 × 10^{-2} M, Figure 3A) there was a combination of both cyclic and higher molecular weight linear polymer. A simple methodology to control the MWD of linear multiblock polymers at high concentrations was to add varying amounts of difunctional X−PSTY−X to monofunctional polySTY (X−PSTY). Figure 5 shows the MWDs of the starting polymer after aminolysis, oxidation, and then reduction when varying the ratio of X−PSTY−X to X−PSTY from 35:1 to 1:1. The MWD at a ratio of 35:1 (Figure 5A) showed a high amount of oxidation (i.e., high molecular weight polymer, curve b) after aminolysis with a M_n and PDI of 8896 and 2.28 (Table 2). Oxidation for 48 h showed a shift to higher molecular weight with an increase in the M_n and PDI (11 630 and 2.83, respectively). Interestingly, this polymer can be readily reduced (curve d) back to the starting polymers with thiol end groups, in which the M_n and PDI were close to that of the starting mono- and difunctional polymers. The MWDs for the lower ratios of X−PSTY−X showed a similar trend.

Table 2 shows that as the ratio of monofunctional polymer, X−PSTY, was increased the M_n after 48 h of oxidation decreased from the initial ratio of 35 to 1 and the PDI also decreased, suggesting that the monofunctional polymer end-capped the multiblocks and thus controlled the MWD. In all cases, after reduction the M_n's and PDIs were close to those of the starting polymers.

Conclusion

A difunctional RAFT agent was used to mediate the living polymerization of styrene to form an α,*ω*-telechelic polystyrene. The telechelic end groups were converted to thiols with the addition of hexylamine, and further oxidation gave either monocyclic polymer chains (i.e., with only one disulfide linkage) or linear multiblock polymers with many disulfide linkages depending on the concentration of polymer used. The more dilute the solution, the greater the chance of cyclization. When the polymer was fed into a solution containing hexylamine, greater than 76% of the number percent was cyclic. Cyclization was also confirmed by the fact that after adding Ellman's reagent little or no free thiols were found in the low molecular weight cyclic peak by UV−vis SEC analysis. At high polymer concentrations, linear multiblock polymers were formed. To control the MWD of these linear multiblocks, monofunctional X−PSTY was added. At the greatest ratio of X−PSTY to X−PSTY−X low M_n and PDI were observed. We have shown that we can control both the structure and MWD using this chemistry, but more importantly such disulfide linkages can be readily reduced back to the starting polystyrene with thiol end groups.

This work could be extended to produce a range of combinations of linear and cyclic polymers, with the possibility of the linear polymers interpenetrating the loops of cyclic structures to produce materials with high tensile strength properties and well-defined break at stress. It is also conceivable that multiblock copolymers from a wide variety of homopolymers can be linked using this methodology and then recycled to the starting homopolymers for use in another application.

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