Anionic Synthesis of Epoxy End-Capped Polymers

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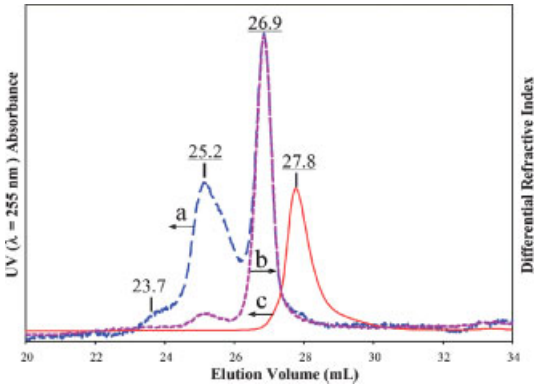
The reaction of living anions of polystyrene (PS) or poly(methyl methacrylate) (PMMA) with epibromohydrin for the synthesis of well-defined epoxy end-functionalized polymers is reported. Polyanions were reacted with an excess of epibromohydrin in tetrahydrofuran (THF) at −78 °C. The functionalities of the resulting polymers were analyzed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), NMR, and size exclusion chromatography (SEC). The epoxy end groups were reacted with 1,1-diphenyl- hexyllithium, and MALDI-TOF MS and NMR before and after this chemical modification were used to determine the presence of the epoxy end groups. The presence of the epoxy end group was confirmed by anionically polymerizing ethylene oxide from these epoxy end group. The formation of a block copolymer due to the epoxy end groups was proved by SEC analysis. The combined MALDI-TOF MS, ^{1}H NMR, and SEC results indicate that epoxy end-capped PS was obtained in quantitative yield. The method was extended to the synthesis of epoxy end-capped PMMA. With this polymer the extent of end-functionalization was high but not quantitative, with non-dimeric byproducts detected by MALDI-TOF MS.



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Introduction

Linear macromolecules having reactive functional group at one end, often referred to "end-functionalized polymers", or both ends, often referred to as "telechelics", are of paramount importance in the tailored synthesis of advanced polymeric materials.[1,2] Such end-functionalized polymers have been extensively used as chain extension and linking agents in preparation of segmented copolymers, cyclic polymers, and many other complex macro-

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molecular architectures.[3–6] In the field of bioengineering, well-defined end-functionalized biocompatible and biodegradable polymers have been demonstrated to be useful site-specific bio-recognition materials or biosensors.[7–9] Furthermore, well-defined end-functionalized polymers can be used to prepare polymer modified surfaces via adsorption and chemical reactions.[10–12] The focus of this paper is to report the quantitative synthesis of epoxy end-functionalized polymers by anionic polymerization. The epoxy end group is a very interesting one because it is not only a reactive functional group (reacts efficiently with anhydride and amine group, thus it is frequently employed to enhance the interfacial binding between incompatible polymers) but also a polymerizable functional group (polymers having epoxy end groups may be classified as ''macromonomers''). The synthesis of high quality epoxy end-functionalized polymers and telechelics is thus an essential step in our current collaboration aimed at the understanding the attachment, self-organization, and properties of polymer-bound surface layers.

A number of methods for the preparation of well-defined epoxy end-functionalized polymers have been reported by a number of different research groups.[13–18] Xie and Sun,[13] Mouzali et al.,[14,15] Jiang and Liang,[16] and Quirk and Zhou[18] have all investigated the reactions of epihalohydrin with living polystyryllithium under different conditions. Xie and Sun reported that the presence of a small amount of tetrahydrofuran (THF) ([THF]/[BuLi] $\approx$ 2) and use of an inverse addition of cyclohexane solution of the living polystyryllithium to an excess of epichlorohydrin (ECH) ([ECH]/[BuLi] $\approx$ 2) at 50 °C gave a maximum yield of epoxide-functionalized PS of only 35%.[13] Mouzali et al. reported that adding the benzene solution of α,ω-dilithiopoly(styrene-isoprene-styrene) to the THF solution of ECH at −30 °C yielded 40% of the epoxy end-functionalized product.[14] These same authors later reported that the reaction of ECH with the same living triblock copolymer end-capped with 1,1-diphenylethylene (DPE) under the same conditions ''leads to epoxy groups at the chain-ends''.[15] Unfortunately, no detailed information was given in their publication regarding the yield or characterization of the resulting polymers. Youqing and Eping reported that end-capping the living polystyryl anion with cyclosulfide propane prior to the reaction with ECH in cyclohexane at 0 °C substantially reduced the extent of side reactions and yielded epoxy end-functionalized PS oligomers at levels as high as 83%.[16] These authors used acid-base titrations where the epoxy end groups react quantitatively with hydrochloric acid, forming chlorohydrin, and the amount of acid consumed was used to calculate the yield of the epoxy end-functionalized polymers. Nakahama and coworkers concluded, based on the results of these prior studies, that polystyryllithium could not react selectively with the haloalkyl functionality of epihalohydrin, thus resulting in the formation of dimeric species.[17] In addition, they suggested that a vicinal position each for halo and epoxy in epihalohydrin might be responsible for the formation of the unfunctionalized polymers. Thus, Nakahama et al. investigated the reaction of 2-bromoethyloxirane, in which the bromine is separated from the epoxy ring by two methylene units as compared to only one in epibromohydrin (EBH), with polystyryllithium in THF at −78 °C.[17] They concluded that quantitative epoxy end-functionalized PS could be obtained by carefully adding the cold THF solution of living polystyryllithium into the THF solution of 2-bromoethyloxirane. If the THF solution of 2-bromoethyloxirane was added to the living polymer solution, a significant amount of the dimeric product (ca. 20%) was observed.[17] Later, Quirk and Zhou re-examined the reaction of ECH with living polystyryllithium in detail and they reported the 91–97% yield of epoxy end-functionalized PS, obtained by capping the polymeric chain end with DPE to form the corresponding polymeric (1,1-diphenylmethyl)lithium, followed by reaction with ECH, in the presence of a small amount of THF at room temperature.[18] Byproducts were clearly detectable in their investigation and quantitative end-functionalization was not achieved.[18]

Based upon the consideration of these literature results, we felt that EBH could prove to be an effective terminating reagent for the synthesis of epoxy end-functionalized polymers, provided the reaction conditions were further optimized. In the end-functionalization reaction of epihalohydrin with living polystyryl anions, the nucleophilic attack of the anions can occur at the halogen containing carbon as well as the epoxy-carbon. Many previous studies have shown that in non-polar solvents the reaction rate of these two completing reactions are similar and the yield of the desired product was low. Quirk and Zhou[18] improved the yield of epoxy end-functionalized PS up to 97% by end-capping the living polymers with DPE and adding 10% THF into benzene, which was the solvent used in their reactions. We believed that using neat THF as the solvent might further increase the reactivity difference between the halo group and the living anionic polymer as compared to epoxide and the same living anionic species. Hence, the ring-opening and dimerization side reactions might be further minimized. Since the living anionic polymers can undergo termination reactions in the presence of THF at higher temperatures, low reaction temperatures must be used. Secondly, as mentioned above Mouzali et al.[14] reported a 40% yield of epoxy end-functionalized polymers by adding the benzene solution of α,ω-dilithiopoly(styrene-isoprene- styrene) to the THF solution of ECH at −30 °C. We thus believed that adding the EBH quickly to the polymer solution at −78 °C might also help suppress the side reactions. It is also germane that EBH is

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commercially available and relatively easier to purify than 2-bromoethyloxirane. Thus, a route based on EBH would be advantageous as compared to the synthetic strategy proposed by Nakahama and coworkers.[17] In this paper, we report the use of matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), NMR spectroscopy, and size exclusion chromatography (SEC) methods to investigate the reaction of living anions of polystyrene (PS) and poly(methyl methacrylate) (PMMA) with EBH for the synthesis of well-defined epoxy end-functionalized polymers.

Experimental Part

Polymerization Procedures

Anionic living polymerizations of styrene-d_8 and methyl methacrylate were conducted using standard all-glass high vacuum techniques.[19–21] Deuterated styrene monomer was used here because the telechelic polymers will be used in a neutron reflectivity study in the next step of our project. An additional advantage of using deuterated monomer in this study is that we can better characterize the end group by proton NMR measurements since the signals raised by the polymer backbone will be absent. Solvents, monomers, terminating reagent EBH, and chemicals employed in the synthesis of initiators [except for 1,3-bis(1-phenylethenyl)benzene (PEB), which was obtained from Dow Chemical, compliments of Steve Hahn, and styrene-d_8, which was purchased from Cambridge Isotopes] were purchased from Aldrich. Solvents and monomers were purified according to the standard published procedures.[19–21] EBH was purified by stirring over CaH_2 overnight on the vacuum line with degassing, then distilled into ampoules. The α,ω-dianionic polystyrene backbone of the telechelic was synthesized using (1,3-phenylene)bis(3-methyl-1-phenylpentylidene)dilithium initiator (DLi) in THF at $-78\,^{\circ}C$. DLi was synthesized in-house by the reaction of *sec*-butyllithium and PEB according to a published procedure.[22] The living PMMA was synthesized in THF at $-78\,^{\circ}C$ using (1,1-diphenylhexyl)lithium as an initiator and lithium chloride as an additive to stabilize the ester-enolate chain ends according to a standard procedure.[23]

End-Functionalization Reactions

In the case of deuterated PS (DPS), purified EBH, neat, was added to the living polymer solution at $-78\,^{\circ}C$ ($[Br]/[Li] \approx 5$). The characteristic deep red color of polystyryllithium in THF was observed to disappear completely immediately upon mixing. The reactor was opened and the cold polymer solution was poured into a large excess of methanol to collect the polymer, which was then dried under vacuum. In the case of PMMA, purified neat EBH was added to the living polymer solution at $-78\,^{\circ}C$ ($[Br]/[Li] \approx 5$) and this mixture was kept at $-78\,^{\circ}C$ for at least 4 h. Due to the lower reactivity of the ester-enolate chain ends as compared to living PS chain ends, the end-functionalization reaction was allowed to continue upon warming to room temperature for about 2 h. Then the reaction mixture was poured into a large excess of hexane to collect the polymer. This polymer was then dissolved in toluene to make a 5% w/v solution, which was cloudy due to the presence of lithium chloride. This solution was filtered and the filtrate was poured into a large excess of hexane, and the polymer was collected and dried under vacuum.

Chemical Modification of The Epoxy End Groups with 1,1-Diphenyl-hexyllithium

70 mg of epoxy end-functionalized telechelic DPS ($\overline{M}_n = 3.5 \times 10^3\ g \cdot mol^{-1}$) was dissolved in ≈10 mL of distilled benzene and charged into an all-glass reactor equipped with three ampoules containing butyl lithium, DPE, and methanol. The butyl lithium solution was prepared in-house by the reaction of butyl chloride and lithium metal in hexanes according to a standard procedure.[21,24] This benzene solution was degassed and approximately 1 mL of pure THF was distilled into the apparatus. Then the apparatus was detached from the high vacuum line by heat-sealing. The butyl lithium and DPE were mixed and a deep red color solution was formed. This solution was added drop-wise to the epoxy end-functionalized polymer until the red color of the living anion remained. This solution was left at room temperature for about 1 d, then degassed methanol was added to protonate the excess living anions. A drop of 1 N HCl solution was added to the solution after it was opened to air. The polymer was then precipitated into excess amount of methanol, and the polymer was dried under vacuum followed by MALDI-TOF MS and NMR measurements.

Anionically Polymerizing Ethylene Oxide from the Epoxy End Group

70 mg of epoxy end-functionalized telechelic DPS ($\overline{M}_n = 3.5 \times 10^3\ g \cdot mol^{-1}$) was dissolved in ≈10 mL of distilled benzene and charged into an all-glass reactor equipped with three ampoules containing ethylene oxide, a THF solution of triphenylmethyl potassium ($Ph_3C^-K^+$), and methanol. The THF solution of $Ph_3C^-K^+$ was prepared in-house by the reaction of triphenylmethane and potassium metal in THF at room temperature. The excess potassium metal was removed by passing the solution through a glass filter. A volume of 30 mL pure THF was distilled into the reactor followed by flame-sealing the apparatus from the high vacuum line. The epoxy end-functionalized polymers were titrated by adding the THF solution of $Ph_3C^-K^+$ drop-by-drop until the characteristic red color of the living anion remained. Then the break-seal of the ethylene oxide ampoule was ruptured and the solution was kept at 50 °C for 6 d to allow for polymerization of the ethylene oxide. The resulting block copolymers were characterized by SEC.

MALDI-TOF MS Analysis

Methods employed were similar to those used in our previous work.[25] A Voyager DE Pro MALDI-TOF MS unit from PE PerSeptive Biosystems (Framingham, MA) was employed to obtain the mass

spectra of the DPS-α,ω-diepoxy and the mono-epoxy end-functionalized PMMA oligomer. Trans, trans-1, 4-diphenyl-1, 3-butadiene was used as the matrix and silver trifluoroacetate (AgTFA) was used as the cationizing reagent for the measurement of DPS-α,ω-diepoxy. For the measurement of mono-epoxy end-functionalized PMMA oligomer, 2,5-dihydroxybenzoic acid was used as the matrix and potassium trifluoroacetate (KTFA) was used as the cationizing reagent. In both cases, solutions of matrix (20 mg $\cdot$ mL^{-1}), polymer (20 mg $\cdot$ mL^{-1}), and cationizing reagent (5 mg $\cdot$ mL^{-1}) were prepared in THF. These solutions were mixed in the volume ratios of matrix/polymer/cationizing reagent of 10:1:1. A volume of 1 μL of the mixture solution was applied to the sample target and the solvent was evaporated by air-drying (the dried droplet method[26]). All the measurements were carried out in positive ion and linear mode. The accelerating voltage was 25 000 V. The mass spectrum displayed in this article is the average result of 128 single-shot spectra. The mass scale was calibrated externally using the peptides: angiotensin-I (M = 1 296.5) and insulin bovine pancreas (M = 5 733.6) (Sigma, St. Louis, MO) as standards.

^{1}H NMR Measurements

^{1}H NMR experiments were performed on a Bruker AMX400 spectrometer (Bruker Instruments, Karlsruhe, Germany). A wide bore Oxford/Spectrospin magnet of 9.4T (400.13 MHz) field strength was used for the reported experiment. Typical ^{1}H parameter settings include temperature = 305 K, relaxation delay = 30 s, number of scans = 16, solvent = deuterated chloroform. The sample concentration is 20 mg $\cdot$ mL^{-1}. The internal standard was the residual proton chloroform signal of deuterated chloroform (7.24 ppm downfield from tetramethylsilane).

Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was used to determine the average molecular weights and molecular weight distributions, $\overline{M}_w/\overline{M}_n$, of the polymer samples with respect to PS standards [Polymer Standards Service (PPS), Germany]. The instrument was equipped with an isocratic pump (Knauer K-501), a UV detector (Knauer UV-K2501), an RI detector (Knauer RI-K2301), and one LinearS and one 100 Å (8 × 600 mm) linear PSS SDV gel columns. PSS WinGPC software was used to acquire and analyze the chromatograms. All samples were run using THF as the mobile phase at a flow rate of 1 mL $\cdot$ min^{-1} at 30 °C.

Results and Discussion

The reaction of polystyryllithium ($\overline{M}_n = 3.5 \times 10^3$ g $\cdot$ mol^{-1}) with excess EBH in THF at −78 °C was first examined using MALDI-TOF MS and the mass spectrum of the epoxy end-functionalized telechelic DPS is displayed in Figure 1. Also shown in this figure is the synthetic scheme used to make this polymer. All peaks displayed in this spectrum are consistent with n repeating units of deuterated styrene (112.16 × n) plus the mass of a silver ion (Ag = 107.87), two end groups (methyloxirane, −C_3H_5O, M = 57.12), and the initiating species [(1,3-phenylene)bis(3-methyl-1-phenylpentylidene), −$C_{30}H_{36}$, M = 396.40]. For example,

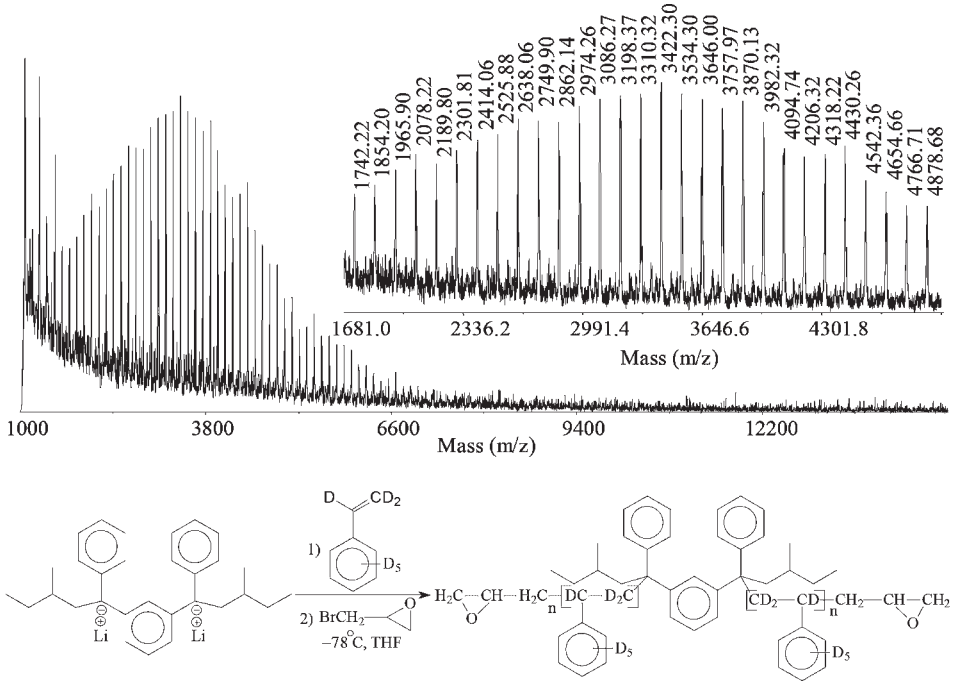

Figure 1. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum of a DPS-α,ω-diepoxy telechelic and the synthetic scheme for making this polymer.

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the mass of such a polymer chain containing 24 repeat units is $112.16 \times 24 + 107.87 + 57.12 \times 2 + 396.40 = \times 2 + 396.40 = 3310.35$. This result matches the peak with mass 3310.32 displayed in Figure 1 very well. No dimeric product is observed in the mass spectrum.

Figure 2 displays the reaction of the epoxy end-functionalized polymer and 1,1-diphenyl- hexyllithium. The MALDI-TOF mass spectra of the starting material (A) and the chemically modified polymer (B) are also shown in this figure. All peak shifts are consistent with the reaction performed. For example, the peak at 4234.77 Da in B resulted from the peak of 3757.97 Da in A plus the mass of the sum of two 1,1-diphenyl-hexane units ($C_{18}H_{22}$, $M = 476.35$).

The ^{1}H NMR spectra of polymers A and B are displayed in Figure 3. Quirk and Zhou reported that resonances at $\delta = 2.90$, 2.72, and 2.45 ppm are the methine and *cis*- and *trans*-methylene protons of the oxirane ring.[18] These signals are clearly observed in Figure 3(A). Notice that these signals disappear completely after the chemical modification with 1,1-diphenyl-hexyllithium.

The epoxy functional groups at the polymer chain ends react efficiently with triphenylmethyl potassium

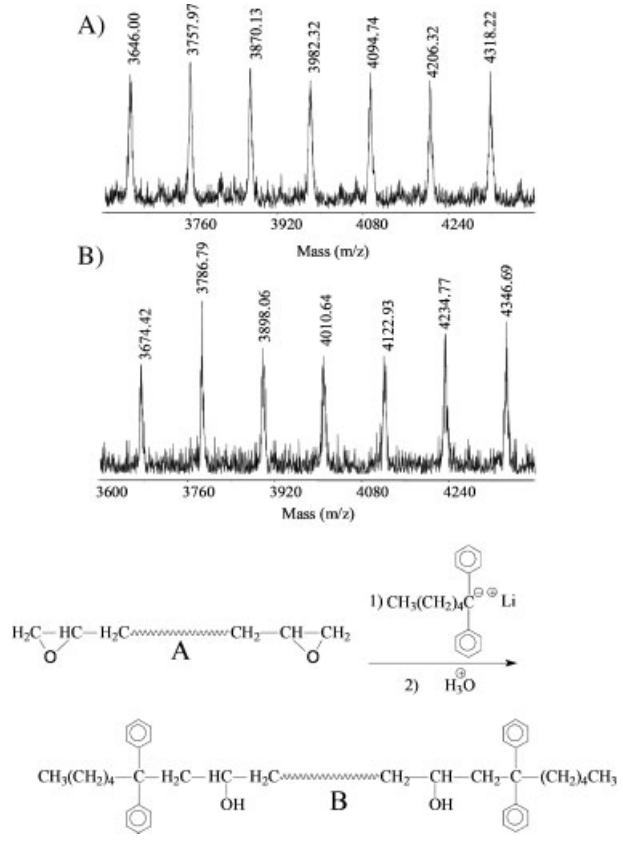

Figure 2. Matrix-assisted laser desorption/ionization time-of-flight mass spectra of (A) DPS-α,ω-diepoxy telechelic and (B) product from the reaction of A and 1,1-diphenyl-hexyllithium. The reaction scheme is also shown in this figure.

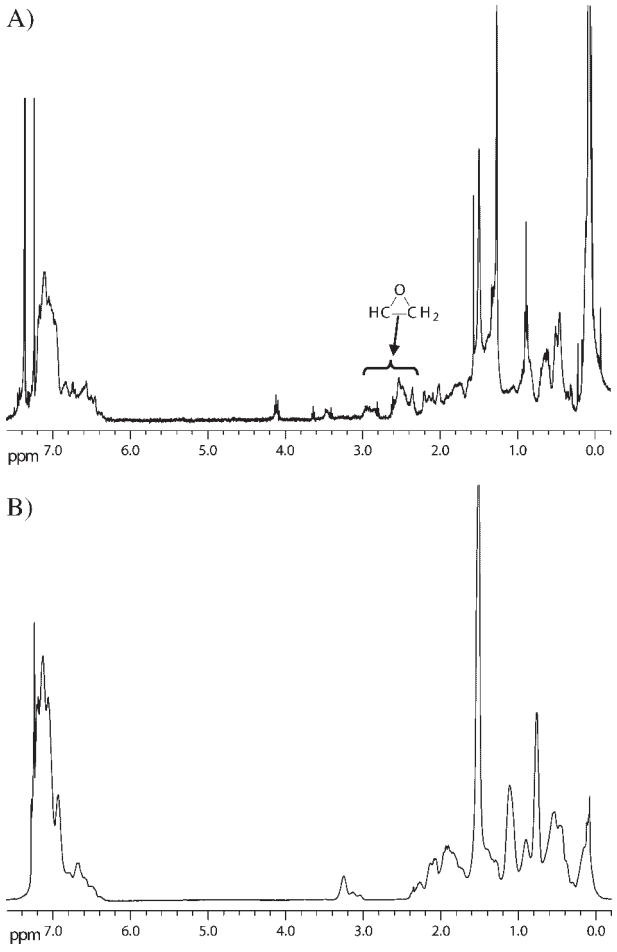

Figure 3. ^{1}H NMR spectra of (A) DPS-α,ω-diepoxy telechelic and (B) product from the reaction of A and 1,1-diphenyl-hexyllithium.

($Ph_3C^-K^+$), creating chain ends that can initiate the living anionic polymerization of ethylene oxide. This provides us with an alternative method of analyzing the functionalities of the epoxy end-functionalized polymers. Here we titrate a sample of DPS-α,ω-diepoxy telechelic ($\overline{M}_n = 3.5 \times 10^3$ g · mol^{-1}) synthesized as above using a THF solution of triphenylmethyl potassium. This solution is deep red in color and will turn colorless upon contact with epoxy groups or any impurity in the reactor that might terminate the anionic polymerization. Thus, this solution itself can be used as indicator of the titration end point. A scheme showing this titration reaction and the anionic polymerization of ethylene oxide is displayed in Figure 4. After the titration, the resulting di-functional macroinitiator was used to polymerize ethylene oxide. A PEO-*b*-DPS-*b*-PEO triblock copolymer should be obtained from this procedure. The excess amount of triphenylmethyl potassium over the titration end point will also polymerize the ethylene oxide monomer and produce PEO homopolymer. The characteristics of this PEO homopolymer should be

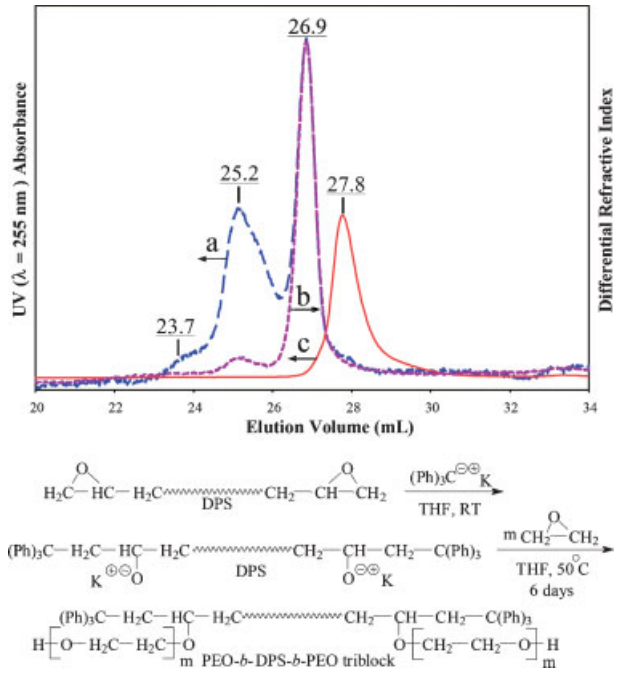

Figure 4. Size exclusion chromatography curves of: UV ($\lambda = 255$ nm) detector response (blue dashed line) of the product from the above scheme, curve a; RI detector response (purple dots) of the same polymer that generated curve a, curve b; and UV detector response (red solid line) of the starting materials (DPS-α,ω-diepoxy telechelic), curve c. Also displayed in this figure is the scheme for the chain extension reaction.

identical to the two outside blocks of the triblock copolymer.

Size exclusion chromatography (SEC) was used to characterize the resulting PEO-*b*-DPS-*b*-PEO triblock copolymer and determine the functionality of the starting materials, which is a α,ω-diepoxy telechelic deuterated PS. Three SEC curves are displayed in Figure 4. Curve a (blue dashed line) is the SEC trace of the polymer after anionic polymerization of ethylene oxide from a UV ($\lambda = 255$ nm) detector and curve b (purple dots) is the SEC trace of the same polymer using an RI detector. Also displayed in this figure is curve c (red solid line), which is obtained from the starting materials using a UV detector. The curves obtained from materials after anionic polymerization of ethylene oxide contain multiple peaks maximized at elution volumes of 23.7, 25.2, and 26.9mL. The number-average molecular weights ($\overline{M}_n$) of the two components with elution volumes of 25.2 and 26.9 mL are 38.4×10^3 g · mol^{-1} and 17.5×10^3 g · mol^{-1}, respectively, according to the calibration curve constructed with PS standards. The fact that the materials elute at 25.2 mL have a $\overline{M}_n$ value slightly higher than twice of the $\overline{M}_n$ of the materials eluting at 26.9 mL indicates that these two polymers are the targeted PEO-*b*-DPS-*b*-PEO triblock and the PEO homopolymer initiated by the excess triphenylmethyl potassium over the titration point. Because these two polymers are synthesized in one pot, the characteristics of the PEO homopolymer should be identical to the two outside blocks of the triblock copolymer. In addition, the low molecular weight distribution and the symmetrical shape of the peak eluting at 26.9 mL indicate that this polymer was produced by living anionic polymerization using triphenylmethyl potassium as initiator. The shape of the peak eluting at 25.2 mL is similar to the shape of the peak eluting at 27.8 mL in curve c, which corresponds to the α,ω-diepoxy telechelic deuterated PS. This also indicates that the material eluting at 25.2 mL is polymer initiated by the macro-initiator obtained from the α,ω-diepoxy telechelic deuterated PS.

Polystyrene is UV active and the DPS segment contains an average of 31 styrene units ($\overline{M}_n = 3.5 \times 10^3$ g · mol^{-1}, $M_0 = 112$ Dalton). Poly(ethylene oxide) is not normally UV active but each PEO chain in our work contains one UV active moiety, which is the triphenylmethyl group from the initiator. Thus the UV detector is sensitive to PS but only slightly sensitive to PEO. In contrast, both PS and PEO are readily detected by the RI detector. The peak at 25.2 mL is much more intense in the UV (curve a) than in the RI (curve b), when the UV and RI peaks at 26.9 mL are normalized to the same intensity. This indicates that the peak at 25.2 mL contains PS segments. This is additional evidence that the peak at elution volume 26.9 mL is PEO homopolymer and the peak at elution volume 25.2 mL is PEO-*b*-DPS-*b*-PEO triblock copolymer. The source of the peak centered at 23.7 mL, present in a very small amount, was not identified. The peak corresponding to the starting materials, a α,ω-diepoxy telechelic deuterated PS, is centered at an elution volume of 27.8 mL in curve c. The absence of signal that is distinguishable from the background at this range in curve a (SEC curves of the PEO-*b*-DPS-*b*-PEO triblock) indicates that there is no unfunctionalized DPS homopolymer in this product, further evidence of the quantitative nature of the epoxy end-functionalization reaction reported herein.

The reaction of the living anion of PMMA with an excess of EBH in THF at -78 °C was examined using MALDI-TOF MS and SEC. To the best of our knowledge, investigation of the synthesis of epoxy end-functionalized PMMA has not been reported in the literature. Figure 5 shows the MALDI-TOF mass spectrum and the synthetic conditions used for a mono-epoxy end-functionalized PMMA oligomer. This spectrum shows the expected peaks as the main products. The *m/z* values in the major distribution of peaks correspond to the K^+ ($m = 39.1$) adducts of PMMA oligomers ($100.12 \times n$) having a diphenylhexyl ($-C_{18}H_{21}$, $m = 237.36$) group at one end and methyloxirane, ($-C_3H_5O$, $m = 57.12$) at the other. For example, the peak with a mass value of 934.19 Da is such a polymer chain containing six repeat units. Dimeric products were not observed in the mass

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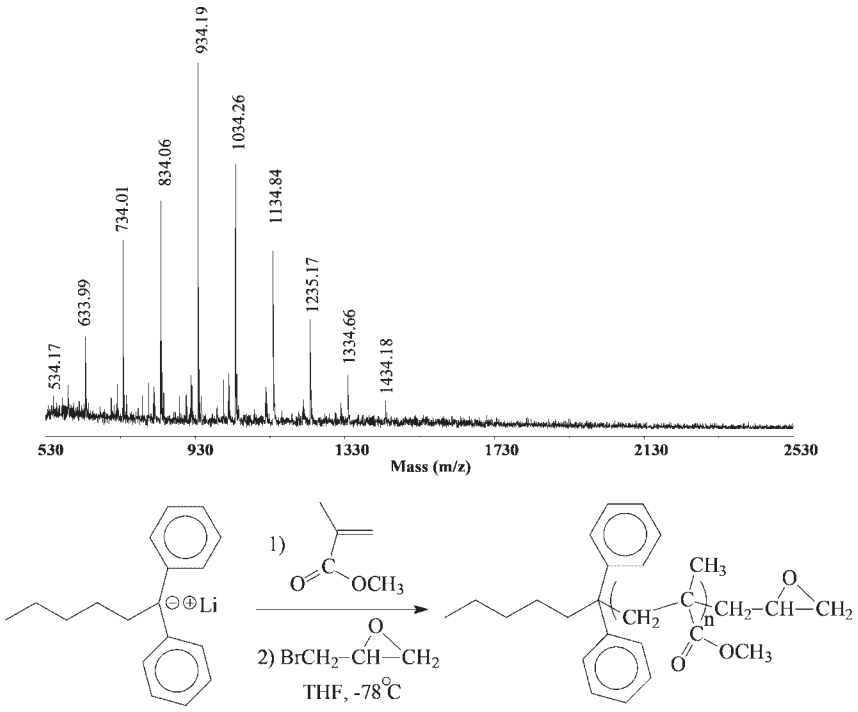

Figure 5. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum of a mono-epoxy end-functionalized PMMA and the scheme for the synthesis of the mono-epoxy end-functionalized PMMA polymer.

spectrum. Some of the less intense peaks reflect the lithium adducts, and others are byproducts that could not be identified. Byproduct from chain end cyclization via intramolecular Claisen condensation was not found in this mass spectrum. This chain end cyclization side reaction occurs when the living polymeric anions are exposed to temperatures higher than −40 °C. The absence of this byproduct may indicate that the end-functionalization reaction was completed at low temperature and allowing the reaction to continue upon warming to room temperature was not necessary.

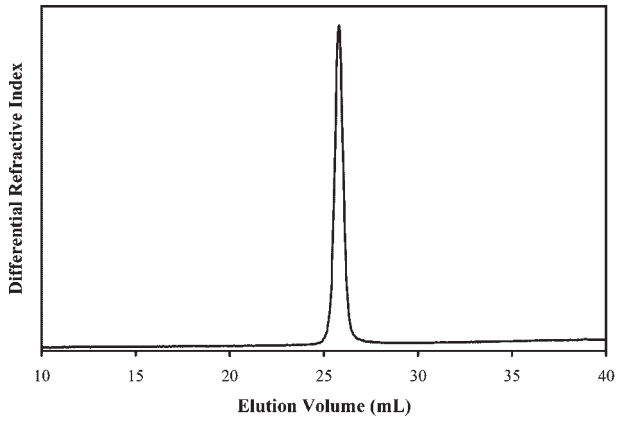

Figure 6. Size exclusion chromatography curve of the epoxy end-functionalized PMMA.

We repeated this reaction using living PMMA anions with higher molecular weight ($\overline{M}_n = 48.3 \times 10^3$ g · mol^{-1}). The SEC chromatogram is displayed in Figure 6. The peak shows a very narrow molecular weight distribution (PDI = 1.05) and it is more than 95% agreeable to a Gaussian distribution. This is an indication of the absence of dimeric products. We conclude that while the strategy reported in this paper gives quantitative results with PS anions, in reactions with PMMA anions some byproducts arising from the reaction of the living anions of PMMA and the epoxy ring in the terminating reagent are also present. The ring-opening side reaction occurs to such a small degree that no dimeric products were detected.

Conclusion

Commercially available EBH can be used as the terminating reagent for the preparation of epoxy end-capped PS in quantitative yield. A highly polar media, e.g. THF, should be used so that the living anionic polymer chains will react selectively with the bromo functionality but not with the epoxy ring in the EBH. Carrying out these reactions at −78 °C can successfully eliminate potential side reactions. Extension of the same strategy to the synthesis of epoxy end-capped PMMA also gave good results although some non-dimeric impurities were detected by MALDI-TOF MS.

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[1] "*Telechelic Polymers: Synthesis, and Applications*", E. J. Goethals, Ed., CRC Press, Boca Raton, FL 1989.
[2] A. Hirao, M. Hayashi, *Acta Polym.* **1999**, *50*, 219.
[3] D. Pantazis, D. N. Schulz, N. Hadjichristidis, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1476.
[4] H. Schlaad, M. Antonietti, *Eur. Phys. J.* **2003**, *10*, 17.
[5] J. Kim, S. Kim, K. Kim, Y. Jin, S. Hong, S. Hwang, B. Cho, D. Shin, S. Im, *Polymer* **2004**, *45*, 3527.
[6] C. A. Orr, J. J. Cernohous, P. Guegan, A. Hirao, H. K. Jeon, C. W. Macosko, *Polymer* **2001**, *42*, 8171.
[7] H. Otsuka, Y. Nagasaki, K. Kataoka, *Langmuir* **2004**, *20*, 11285.
[8] T. Ouchi, T. Uchida, H. Arimura, Y. Ohya, *Biomacromolecules* **2003**, *4*, 477.
[9] H. Hayashi, M. Iijima, K. Kataoka, Y. Nagasaki, *Macromolecules* **2004**, *37*, 5389.
[10] E. Eastwood, M. D. Dadmun, *Macromolecules* **2002**, *35*, 5069.
[11] M. D. Dadmun, "The Compatibilization of Polymer Blends with Linear Copolymers: Comparison between Simulation and Experiment", in: *Computational Studies, Nanotechnology, and Solution Thermodynamics of Polymer Systems*, Kluwer Academic, New York 2000.
[12] E. Eastwood, M. D. Dadmun, *Polymer* **2002**, *43*, 6707.
[13] H. Xie, W. Sun, "*Advances in Polymer Synthesis*", B. M. Culbertson,J. E. McGrath, Eds., Plenum Press, New York 1985, p. 461.
[14] M. Mouzali, J. Lacoste, M. J. M. Abadie, *Eur. Polym. J.* **1989**, *25*, 491.
[15] M. Mouzali, J. Lacoste, M. J. M. Abadie, *Eur. Polym. J.* **1992**, *28*, 1241.
[16] Y. Jiang, E. Liang, *Polymer* **1992**, *33*, 5076.
[17] K. Takenaka, A. Hirao, S. Nakahama, *Polym. Internat. l* **1995**, *37*, 291.
[18] R. P. Quirk, Q. Zhou, *Macromolecules* **1997**, *30*, 1531.
[19] M. Morton, L. J. Fetters, *Rubber Chem. Technol.* **1975**, *48*, 359.
[20] N. Hadjichristidis, H. Iatrou, S. Pispas, M. Pitsikalis, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3211.
[21] D. Uhrig, J. W. Mays, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 6179.
[22] H. Iatrou, J. W. Mays, N. Hadjichristidis, *Macromolecules* **1998**, *31*, 6697.
[23] D. Baskaran, *Prog. Polym. Sci.* **2003**, *28*, 521.
[24] N. Hadjichristidis, M. Pitsikalis, S. Pispas, H. Iatrou, *Chem. Rev.* **2001**, *101*, 3747.
[25] H. Ji, W. K. Nonidez, R. C. Advincula, G. D. Smith, S. M. Kilbey, II.M. D. Dadmun, J. W. Mays, *Macromolecules* **2005**, *38*, 9950.
[26] M. Karas, F. Hillenkamp, *Anal. Chem.* **1988**, *60*, 2299.

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