

Synthesis and Characterization of Polystyrene Oligomers with Several Pendent Epoxy Groups

Jian Zhang,¹ Hui Huang,¹ Yong Guan,¹ Da-Fu Wei,¹ Fu-Zeng Hu,¹
An-Na Zheng,¹ Hui-Ning Xiao²

¹Key Laboratory for Ultrafine Materials (Ministry of Education), School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

²Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

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ABSTRACT: Living polystyryl lithium was synthesized by anionic polymerization under the protection of argon at normal pressure, and styrene, toluene, tetrahydrofuran, and *n*-butyllithium were used as a monomer, solvent, polar reagent, and initiator, respectively. Then, polystyrene oligomers containing several pendent epoxy groups with well-defined structures and narrow molecular weight distributions (weight-average molecular weight/number-average molecular weight < 1.1) were prepared by the reaction of polystyryl lithium with glycidyl methacrylate. The prepared oligomers were characterized with gel permeation chromatography, Fourier transform infrared spectroscopy, ¹H-NMR, and the hydrochloric acid/dioxane

argentometric method. The effects of the glycidyl methacrylate dosage, molar mass of polystyrene precursors, copolymerization time, and temperature on the content of side epoxy groups were also investigated. The results confirm that 1,1-diphenylethylene-end-capped polystyryl carbanion could initiate glycidyl methacrylate in toluene in the presence of lithium chloride and a small amount of tetrahydrofuran, and the content of the side epoxy groups could be adjusted. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2566–2574, 2010

Key words: anionic polymerization; copolymerization; oligomers; polystyrene

INTRODUCTION

Polystyrene has been extensively used in domestic refrigerators, packaging, medical equipment, house wares, photographic film, compact disc cases, and many other industrial applications. However, this material suffers from several drawbacks (e.g., low impact strength, poor weather fastness, chemical resistance) that strongly limit its application. To overcome these drawbacks, efforts have been made to modify polystyrene, including graft and block copolymerization modification. For example, functional polystyrene can be achieved via block copolymerization. The representative reactive groups introduced to the side chain of the polymers involve epoxy, vinyl, carboxyl, hydroxyl groups, and so on. It has been well known that epoxy groups are relatively stable and have a strong inclination to react with some compounds, such as alcohol, amines, acids and alkalis; this results in the synthesis of various grafting or block copolymers. A number of

articles and patents have been published regarding this approach.^{1–7}

Glycidyl methacrylate (GMA) is an interesting monomer with three reactive functional groups, carbon–carbon double bonds, carbonyl groups, and epoxy groups. The methacrylic carbanion of this monomer exhibits a strong tendency to react with the carbonyl and epoxy groups. Anionic initiators are also able to induce the ring-opening polymerization of oxirane under specific experimental conditions, which depend mainly upon the counterions used. However, the initiation of the ring-opening reaction still occurs, even under the chosen experimental conditions (low temperature and Li counterion). The resulting alkoxide sites are not sufficiently nucleophilic to attack a methacrylic unsaturated carbon double bond.⁸ Possible side reactions of GMA occur on the carbonyl or oxirane group. If the carbanions attack the carbonyl group and oxirane group of GMA, this will result in the formation of *tert*-hydroxyl group and primary hydroxyl group, respectively. As a result, the anionic polymerization of GMA is generally performed at extremely low temperature (e.g., –78°C) to reduce or eliminate side reactions.

GMA-based homopolymers and copolymers containing epoxy groups are potential functional materials that have various applications. For instance, they can be used as polymeric reagents. The high

Correspondence to: An-Na Zheng (zan@ecust.edu.cn).

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chemical reactivity of the epoxy groups with various reagents provides novel approaches to prepare numerous multifunctional polymers.

The preparation of well-defined block copolymers requires that every individual step, including separated polymerization reactions, must be highly efficient and carefully controllable. It is obvious that these synthetic strategies involve special care in their design and application. Living anionic polymerization is one of the most reliable and useful methods for the synthesis of well-defined block copolymers. For example, when the styrene monomers are completely consumed by the anionic polymerization (the rate of conversion could easily reach 100% in a few minutes), the polystyrene oligomer containing reactive groups could be further prepared by the addition of other monomers with two functional groups into the living system. Theoretically, the molecular weight, molecular structure, and sequence distribution of the final products could be ideally controlled by anionic polymerization.

There have been several publications regarding the anionic polymerization of block copolymers containing GMA segments.⁸⁻¹⁶ Hild and Lamps¹² investigated the sequential anionic polymerization of styrene and GMA in tetrahydrofuran (THF) and obtained diblock and triblock copolymers with well-controlled structures and fairly low polydispersities. The anionic polymerization of (meth)acrylates is commonly performed in THF, for it allows the polymerization to carry on in a living manner. THF, being a polar reagent, accelerates the polymerization rate, but it also limits the usage range of polymerization temperature for its low boiling point (66°C at 760 Torr). This requires the polymerization to be performed under very low temperatures (usually < -55°C under normal pressure). The relative short polystyrene block is easily dissolved in toluene. In addition, with the boiling point of the solvent taken into account, toluene (bp = 110.6°C under normal pressure) is selected to serve as the hydrocarbon solvent for the copolymerization. In this article, a new synthetic approach is reported, which could allow the number of epoxy groups to be adjusted appropriately to address the practical requirements. There were three steps in the preparation. First, the monomer was dissolved in toluene instead of THF, for toluene was more convenient to implement the anionic polymerization of styrene under a relatively higher temperature (>0°C). Second, polystyrene precursors were prepared at 0–5°C in the presence of lithium chloride (LiCl) as the ligand, and then, the polystyrene precursors were end-capped with 1,1-diphenylethylene (DPE). Finally, GMA monomers were incorporated into the system at a low temperature (ca. -65°C) to form polystyrene oligomers containing pendent epoxy groups.

In this study, polystyrene oligomers containing several side epoxy groups with narrow molecular weight distributions were preliminarily prepared via the copolymerization of polystyryl lithium (PSLi) with GMA. In this study, we mainly focused on simplifying the copolymerization procedure and ensuring that the pendent epoxy groups of GMA remained unaffected during the preparation. Another objective was to control the average number of pendent side epoxy groups for versatile applications.

EXPERIMENTAL

Materials

Solvent

Toluene (analytical reagent; Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) was used as a polymerization solvent. To obtain hyperpure toluene, two successive distillations were conducted. In the first step, toluene was distilled over freshly crushed calcium hydride (CaH₂). It was further distilled from a few drops of a *n*-butyllithium (*n*-BuLi) dilute solution under reduced pressure immediately before use.

THF (analytical reagent; Shanghai Chemical Reagent Co., Ltd., Shanghai, China) was dried with CaH₂ under refluxing for more than 24 h under an atmosphere of argon. Then, it was distilled again and refluxed with sodium wire for 10 h, and finally, it was distilled from a fresh benzophenone-sodium adduct dilute solution.⁸ THF was used as a solvent for LiCl and as polar additive for the anionic synthesis of polystyrene precursors.

Methanol (HPLC; Shanghai Chemical Reagent Co.), for the quenching of the polymerization reactions, was degassed on a vacuum line several times before distillation and stored in a tight Schlenk vessel. Absolute ethanol (analytical reagent; Shanghai Chemical Reagent Co., Shanghai, China), for the precipitation of polymers, was used as received. Cyclohexane (analytical reagent; Jiangsu Yangnong Chemical Reagent Co., Ltd., Yangzhou, China), for the precipitation, was also used as received.

Monomers

Styrene (analytical reagent; Shanghai Lingfeng Chemical Reagent Co.) was dried over calcium chloride (CaCl₂) for 24 h. The inhibitor in styrene was eliminated by a first distillation over CaH₂ under reduced pressure. It was vacuum-distilled again over sodium wire every time before use.

GMA (from Dow Chemical Co., 99.4%) was dried over CaH₂ with magnetic stirring for more than 24 h and vacuum-distilled twice slowly over pure CaH₂ powder; the first and the last fractions were removed. The middle fraction was stored in a

Schlenk vessel at a low temperature and was distilled with a small amount of (1,1-diphenylhexyl)-lithium (DPHLi) before use.¹⁶

DPE (99%; Acros Organics, Geel, Belgium) was distilled twice over sodium wire.

Initiators

n-BuLi (Acros; a 2.5M solution in hexane) was diluted with purified hexane, and its concentration (1.0M) was determined by Gilman double titration.¹⁷

DPHLi was used to refine the relevant monomers and solvents. It was prepared by the *in situ* reaction of *n*-BuLi and DPE in THF at -30°C .

LiCl (99%; Acros) was used as received. It was dissolved in THF to form a saturated solution and was titrated by *n*-BuLi until a reddish color appeared after the addition of a few drops DPE.

Polymerization

Synthesis of the polystyrene precursors

The anionic polymerization of styrene initiated by *n*-BuLi was carried out in toluene at $0\text{--}5^{\circ}\text{C}$ for 1 h with the protection of argon under normal pressure in a glass reactor equipped with a magnetic stirrer. An oven-dried, toluene-rinsed flask was prepared first. After 48 mL of toluene, 12 mL of styrene, and 3.54 mL of THF (the molar ratio of THF to living sites was 10 : 1, and the volume ratio of toluene to THF was 1 : 0.074) were injected into the flask with dry syringes, the flask was cooled to 0°C immediately in an ice-salt bath. Then, a few drops of an *n*-BuLi dilute solution (0.3M in hexane) were added slowly into the system to neutralize the remaining protonic impurities with relatively vigorous magnetic stirring. After that, a certain volume (dependent on the desired molar mass of the polystyrene precursors) of the *n*-BuLi solution was added at once into the flask under vigorous stirring. The reaction mixture immediately turned a deep red color during the process of the addition. The characteristic red color indicated the formation of polystyryl carbanion. The reaction temperature was kept at approximately 0°C to eliminate the possible chain-transfer reaction in toluene, and the reaction was maintained to last for 1 h. A portion of living polystyrene precursor (1.5 mL) was withdrawn to an attached receiver and quenched by the addition of a small amount of methanol to determine the molecular weight and polydispersity index of the homopolymer by gel permeation chromatography (GPC).

Synthesis of the DPE-end-capped polystyrene precursors

A 1.2-fold molar excess of DPE was added to the remaining reaction mixture; this instantly turned the

solution deep red. The reaction was allowed to keep stirring for 15 min to ensure the complete conversion of PSLi into DPE-end-capped PSLi. The resulting DPE-end-capped PSLi was a dark red product.

Synthesis of the polystyrene oligomer

The calculated volume of GMA (the calculated molar ratio of GMA to living sites ranged from 3 : 1 to 10 : 1) was incorporated into DPE-end-capped PSLi all at once instead of dropwise under efficient stirring beneath -70°C so that initiation would proceed immediately. The reaction medium turned from deep red to faint yellow, the characteristic color of the methacrylic anions. Once the addition was complete, the reaction temperature was raised to -65°C and kept for a desired time. The reaction was terminated with degassed methanol, and the product was precipitated in a large excess of ethanol. The obtained oligomers were vacuum-dried overnight at 50°C until a constant weight was reached. To remove the excess DPE, fractionation was performed by the addition of methanol to a 1% solution of polymer in cyclohexane.

Characterization of the polystyrene precursors and poly(styrene-glycidyl methacrylate)

GPC

The molecular weight and molecular weight distribution of the oligomers were determined with a Waters 515 gel permeation chromatograph (Wyatt Technology Co., Santa Barbara, USA). The measurements were carried out with THF as an eluent at 30°C with a flow rate of 1.0 mL/min, and the standard styrene-divinylbenzene copolymers were used in the GPC columns. The instrument was calibrated with polystyrene standards (Polymer Laboratories, Palo Alto, USA). Samples [number-average molecular weight (M_n) = 2000–15,000 g/mol] were prepared with a concentration of about 0.01 g/mL in THF.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the oligomers were recorded by a Nicolet Magna-IR500 (Thermo Fisher Scientific Inc., Waltham, USA) infrared spectrophotometer (Bruker Co., Ettlingen, Germany). Thin films of the oligomers on KBr salt plates were prepared for testing. Thin films of the samples were prepared by dissolution of the polymer (ca. 200 mg) in chloroform (2 mL) followed by deposition on the KBr salt plates. The samples were scanned at frequencies from 400 to 4000 cm^{-1} , and the number of scan times was 32. The resolution was set at 2 cm^{-1} .

^1H -NMR spectroscopy

^1H -NMR spectra of the oligomers were recorded in CDCl_3 with a Bruker AVANCE DRX500 NMR

spectrometer (Bruker Co., Ettlingen, Germany). Tetramethylsilane was added to the deuterated solvent as an internal standard. Samples were prepared by dissolution of 200 mg of polymer in 1.0 mL of the solvent [deuterated chloroform (CDCl_3)].

^{13}C -NMR spectroscopy

^{13}C -NMR spectra (13,000 scans at 125 MHz with (enter value for pulse sequence parameter (delay)) $d_1 = 6$ s) were also obtained on the Bruker AVANCE DRX500 NMR spectrometer.

Chemical titration of epoxy groups

The content of side epoxy groups herein, which means the molar ratio of epoxy groups to the oligomers in the polystyrene oligomers, was obtained via a known argentimetric method for epoxy group detection.¹⁸ The content of side epoxy groups was calculated with the following equation:

Content of side epoxy groups

$$= \frac{(BN - bn) - (SN - sn)}{1000W} M_n$$

where B is the volume of silver nitrate used in titrating the blank sample (mL), S is the volume of silver nitrate used in titrating the oligomer (mL), N is the normality of the silver nitrate solution, b is the volume of ammonium thiocyanate used in titrating the blank sample (mL), s is the volume of ammonium thiocyanate used in titrating the oligomer (mL), n is the normality of ammonium thiocyanate, W is the weight of the oligomer (g), and M_n is the number-average molecular weight of the oligomer.

RESULTS AND DISCUSSION

Analysis of the GPC chromatogram

The molecular weight of the polystyrene oligomers was analyzed by GPC. A typical GPC profile of the products is shown in Figure 1. Figure 1(B) is the curve of the corresponding polystyrene precursor [S-D-508; $M_n = 2679$ g/mol, weight-average molecular weight (M_w) = 2787 g/mol, $M_w/M_n = 1.041$]. After copolymerization, a slight increase in the molecular weight was observed. M_n of the target product [S-G-508; Fig. 1(A)] was 3703 g/mol with a narrow molecular weight distribution ($M_w/M_n = 1.104$; see Fig. 1). Both M_n values of the two products were satisfactorily in agreement with the theoretical values calculated from the molar ratio of the monomers to the initiator, and the molecular weight distribution was very narrow; this demonstrated that the anionic polymerization proceeded in a living mode. If there

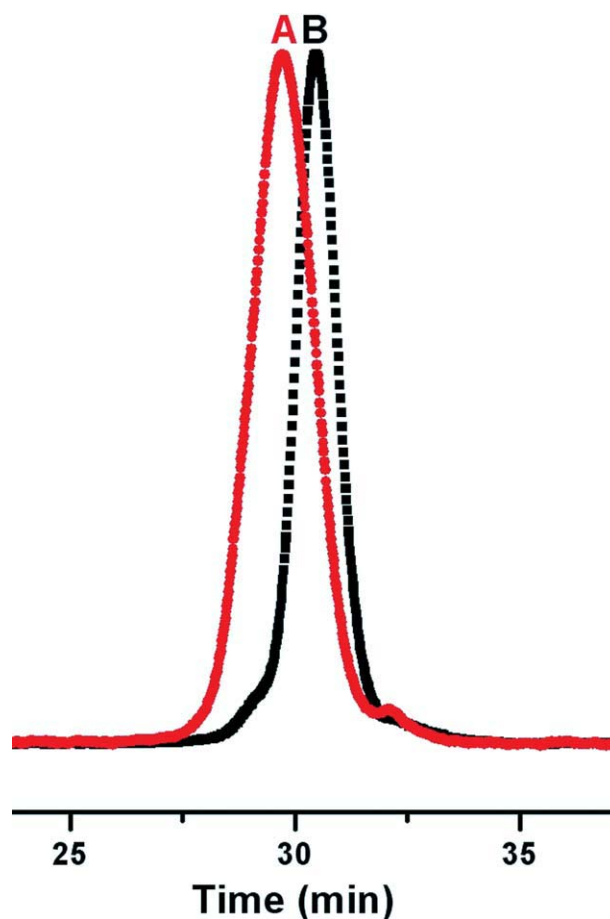


Figure 1 GPC profiles of (A) the polystyrene oligomer and (B) the polystyrene precursor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was, in the side reaction, carbanions attacking the carbonyl group or oxirane, there should have been lower or higher molecular weight side products might appear in GPC curve. From GPC curves, there was nothing to reveal the presence of lower and higher molecular weight side products, confirming the absence of side reactions of carbonyl and epoxy groups.

The results attained with GPC were semiquantitative because the mass responses detected for some calibration compounds were too widespread. The molar mass of the GMA segments per macromolecular chain was able to be determined semiquantitatively by the subtraction of M_n of the polystyrene precursor from M_n of the corresponding polystyrene oligomer. In addition, the deviation of the experimental value of the molar mass of the polystyrene precursor from its theoretical value had a significant effect on the molar mass error of the GMA segments. This was because the amount of GMA incorporated was based on the calculated value from the moles of polystyrene precursor. Therefore, it was important to ensure the narrow molecular weight distribution of the polystyrene precursors and the complete conversion of the

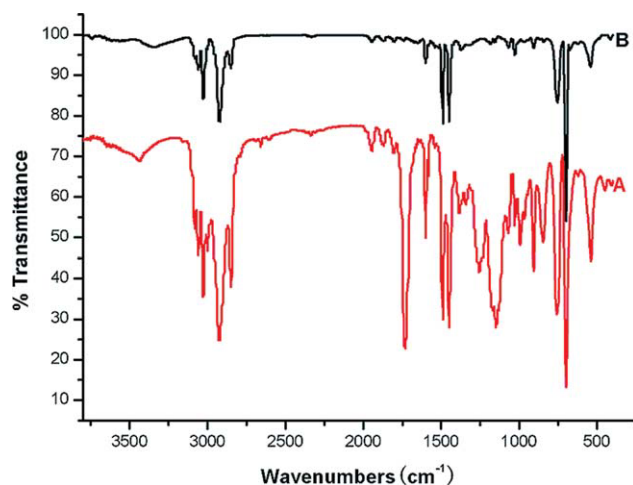


Figure 2 FTIR spectra of (A) the polystyrene oligomer and (B) the polystyrene precursor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polystyrene monomers to minimize the deviation of the average number of GMA segments.

Analysis of the FTIR spectra

Typical FTIR spectra of a polystyrene oligomer (S-G-508) and a polystyrene precursor (S-D-508) are shown in Figure 2(A,B), respectively. No obvious absorbance was observed at 1620 and 1680 cm^{-1} in both spectra, which indicated the absence of carbon double bonds in the polystyrene oligomers. The GMA segments in the products was confirmed by the presence of the characteristic band at 1732 cm^{-1} , corresponding to saturated ester's carbonyl group, which differs from unsaturated ester's carbonyl group with a characteristic band at 1722 cm^{-1} of the GMA monomer. This also can be used to verify the absence of unreacted GMA monomer embedding in the polystyrene oligomers. The absorption peaks around 1253, 912, and 861 cm^{-1} observed in the FTIR spectrum of Figure 2(A) confirmed the presence of epoxy groups. As was men-

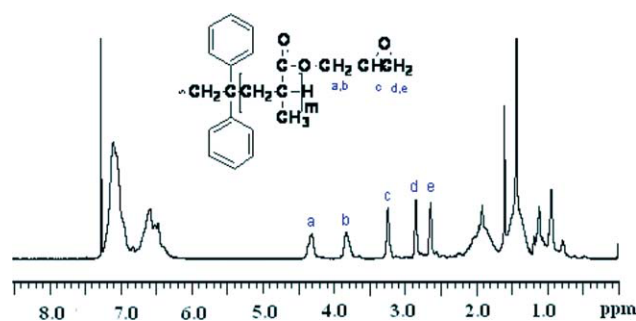


Figure 3 $^1\text{H-NMR}$ spectrum of the polystyrene oligomer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tioned previously, the side reaction of carbonyl (or oxirane) with carbanions would result in the formation of hydroxyl groups. The adsorption band of hydroxyl group might be identified with ease in the FTIR spectrum. However, there was no obvious absorption band around 3433 cm^{-1} ; this indicated that the oxirane ring-opening reaction did not occur during the copolymerization.

Analysis of the $^1\text{H-NMR}$ spectrum

Further characterization was conducted with $^1\text{H-NMR}$, which provided structural information about the backbone and side groups of the polystyrene oligomers. A typical $^1\text{H-NMR}$ spectrum of the polystyrene oligomers (sample S-G-508) is shown in Figure 3. The chemical shifts (δ) at 1.43 and 1.59 ppm were assigned to the $-\text{CH}_2-$ protons of both the styrene and GMA units, and those at 1.87 and 2.05 ppm were assigned to the $-\text{CH}-$ protons of styrene units. The chemical shifts around 6.46 and 7.11 ppm were assigned to the aromatic protons of benzene rings, whereas the shift at 7.24 ppm was assigned to the protons of CDCl_3 . In the $^1\text{H-NMR}$ spectrum, the chemical shifts at 2.65 ppm [Fig. 3(e)] and 2.84 ppm [Fig. 3(d)] were attributed to the $-\text{CH}_2-$ protons, and that at 3.24 ppm [Fig. 3(c)] was attributed to the $-\text{CH}-$

TABLE I
Effect of the GMA Dosage on the Content of Side Epoxy Groups of the Polystyrene Oligomers

Sample ^a	M_{th} ^b	M_n ^c	M_w ^c	M_w/M_n ^c	$[\text{GMA}]/[n\text{-BuLi}]$ ^d	$([\text{GMA}]/[\text{PSLi}])_H$ ^e	$([\text{GMA}]/[\text{PSLi}])_T$ ^f
S-G-703	4500	5215	5642	1.08	5 : 1	5.24	5.38
S-G-508	2500	3703	4090	1.10	7 : 1	6.85	6.76
S-G-729	4500	5563	6253	1.12	8 : 1	8.59	8.16
S-G-730	5000	6696	7532	1.12	10 : 1	10.91	10.72

^a All samples were prepared at -65°C with $n\text{-BuLi}$ in the presence of a small amount of LiCl . The concentration of styrene in toluene was 20% (v/v), the $[\text{THF}]/[n\text{-BuLi}]$ ratio was 10 : 1, and the copolymerization time was 0.5 min.

^b Theoretical value of the molecular weight (calculated from the molar ratio of the monomer to the initiator).

^c Experimental values (determined by GPC).

^d Molar ratio of GMA to $n\text{-BuLi}$.

^e Average number of GMA segments in one copolymer chain (determined from $^1\text{H-NMR}$ spectra).

^f Experimental value of the average number of GMA segments in one copolymer chain (determined by chemical titration).

TABLE II
Effects of the Copolymerization Temperature on the Content of Side Epoxy Groups of the Polystyrene Oligomers

Sample ^a	Copolymerization temperature (°C) ^b	M_n	M_w	M_w/M_n	$([GMA]/[PSLi])_H^c$	$([GMA]/[PSLi])_T^d$
S-G-605	-60	3556	4000	1.12	6.02	6.46
S-G-508	-65	3703	4090	1.10	6.85	6.76
S-G-614	-69	3784	4268	1.13	7.63	7.84
S-G-615	-74	3679	4157	1.13	6.89	7.12

^a All samples were prepared in the presence of a small amount of LiCl. The concentration of styrene in toluene was 20% (v/v), the [THF]/[*n*-BuLi] ratio was 10 : 1, the [GMA]/[*n*-BuLi] ratio was 7 : 1, and the copolymerization time was 0.5 min.

^b Temperature at which GMA was added to the DPE-end-capped polystyrene precursors.

^c Average number of GMA segments in one copolymer chain (determined from ¹H-NMR spectra).

^d Experimental value of the average number of GMA segments in one copolymer chain (determined by chemical titration).

protons of epoxy rings. The two peaks at 3.79 ppm [Fig. 3(b)] and 4.34 ppm [Fig. 3(a)] were assigned to the $-\text{CH}_2-$ protons next to the epoxy group.¹²⁻¹⁴ The peaks (ca. 5.6 and 6.8 ppm) attributed to the protons of the carbon double bonds were not observed in the spectrum; this indicated the absence of the protons corresponding to the methacrylic unsaturation. The content of side epoxy groups was also determined from the spectrum according to the method described in ref. 12. The results are listed in Tables I-IV.

Analysis of the ¹³C-NMR spectrum

Further evidence for the detailed carbon structural information of oligomers was provided by ¹³C-NMR analysis. The ¹³C-NMR spectrum of sample S-G-508 is shown in Figure 4. The carbons of particular interests were the carbons attached to the $-\text{O}-\text{CH}_2-$ group on GMA (10, 12, and 13). The characteristic weak signal at $\delta = 176.85$ ppm was assigned to the carbonyl group on GMA. Each of the particular carbons from the oxirane group has a unique chemical shift in the region between $\delta = 44.55-45.82$ ppm and $\delta = 49.49$ ppm.¹⁹ The chemical shift at $\delta = 66.58$ ppm corresponded to the $-\text{CH}_2-$ adjacent to the oxirane ring. No signal at $\delta = 66.58-70$ ppm, corresponding to the carbon of $-\text{CH}-\text{OH}$, was observed; this indicated that GMA underwent selective anionic polymerization of carbon double bonds in the coex-

istence of DPE and LiCl. No side product of the ring-opening reaction of the oxirane ring was spotted in the ¹³C-NMR spectrum.

According to the previous analysis, the possible reaction mechanism was that DPE-end-capped polystyryl carbanion mainly attacked the β carbon atom of the carbon double bonds in GMA and broke the double bonds to form the α carbanion. Then, the α carbanion initiated another GMA monomer to induce the addition polymerization. Namely, GMA was initiated by the macroinitiator (PSLi). In this way, the polystyrene oligomer, containing several untouched side epoxy groups, was prepared (see Scheme 1; the maximum value of *m* was 10 in our experiments). The polydispersity values of these products were much lower than those reported by Hild and Lamps,¹² and the experimental conditions were much more moderate.

Factors influencing the content of side epoxy groups

Effect of the GMA dosage on the content of side epoxy groups

The content of side epoxy groups of the polystyrene oligomers was analyzed by chemical titration (hydrochloric acid/dioxane argentimetric method). The results are listed in Tables I-IV. The effect of GMA dosage on the content of side epoxy groups is listed in

TABLE III
Effect of the Copolymerization Time on the Content of Side Epoxy Groups of the Polystyrene Oligomers

Sample ^a	Copolymerization time (min)	M_n	M_w	M_w/M_n	$([GMA]/[PSLi])_H^b$	$([GMA]/[PSLi])_T^c$
S-G-508	0.5	3703	4090	1.10	6.85	6.76
S-G-704	1.5	4968	5359	1.08	6.77	6.83
S-G-705	2.0	5616	6009	1.07	7.85	7.93
S-G-706	2.5	5580	5989	1.07	7.60	7.84
S-G-804	5.0	5557	6327	1.14	7.94	7.56

^a All samples were prepared at -65°C in the presence of a small amount of LiCl. The concentration of styrene in toluene was 20% (v/v), the [THF]/[*n*-BuLi] ratio was 10 : 1, and the [GMA]/[*n*-BuLi] ratio was 7 : 1.

^b Average number of GMA segments in one copolymer chain (determined from ¹H-NMR spectra).

^c Experimental value of the average number of GMA segments in one copolymer chain (determined by chemical titration).

TABLE IV
Effects of the Molecular Weights of the Polystyrene Precursors on the Content of Side Epoxy Groups of the Polystyrene Oligomers

Sample ^a	M_{th}^b	M_n	M_w	M_w/M_n	[GMA]/[<i>n</i> -BuLi]	[(GMA)/[PSLi)] _H ^c	[(GMA)/[PSLi)] _T ^d
S-G-508	3,816	3,703	4,090	1.10	7 : 1	6.85	6.76
S-G-515	4,816	4,448	4,902	1.10	6 : 1	6.67	6.79
S-G-516	6,316	5,987	6,444	1.08	7 : 1	6.95	6.83
S-G-517	9,100	8,601	9,038	1.05	8 : 1	7.75	7.56
S-G-522	12,168	12,160	13,120	1.08	15 : 1	15.81	15.58

^a All samples were prepared at -65°C in the presence of a small amount of LiCl. The concentration of styrene in toluene was 20% (v/v), the [THF]/[*n*-BuLi] ratio was 10 : 1, and the copolymerization time was 0.5 min.

^b Theoretical value of the molecular weight (calculated from the molar ratio of the monomer to the initiator).

^c Average number of GMA segments in one copolymer chain (determined from $^1\text{H-NMR}$ spectra).

^d Experimental value of the average number of GMA segments in one copolymer chain (determined by chemical titration).

Table I. The content of side epoxy groups increased with increasing GMA dosage, and the measured content value of side epoxy groups was close to the theoretical value. This result also confirmed that the addition polymerization of GMA with DPE-end-capped PSLi was an effective reaction achieved by the opening of the double bonds. Therefore, the average number of side epoxy groups was preliminarily adjusted by a change in the molar ratio of GMA to the polystyrene precursors (<10) according to the actual need. This followed the rule of anionic living polymerization, but as soon as the GMA dosage accrued, the copolymerization would have become complicated for the poor solubility of poly(glycidyl methacrylate) (PGMA) in toluene. Future work will be extended to investigate the influence of GMA dosage when the molar ratio of GMA and polystyrene precursors is much larger than 10.

Effect of the copolymerization temperature on the content of side epoxy groups

A previous study²⁰ focused on the reaction of GMA and polystyrene precursors at various temperatures ($>0^\circ\text{C}$). In this study, we investigated the effect of the reaction temperature on the content of epoxy groups. The result showed a broad molecular weight distribution (ca. 1.3) on the GPC profiles and a comparatively large deviation in the molecular weight between the theoretical and measured values. The content of epoxy groups decreased with increasing reaction temperature at an identical molar ratio of GMA to polystyrene precursors. The ring-opening reaction of the oxirane rings was confirmed by the FTIR spectra. This could be used to explain the deviation between the theoretical and measured values of the content of epoxy groups. To eliminate the side reactions derived from GMA and to prepare polystyrene oligomers with well-defined structures, well-controlled molecular weights, and narrow molecular weight distributions, all of the experiments were performed at a low temperature (beneath -60°C). The effect of the copolymerization temperature on

the content of epoxy groups is shown in Table II. Ruckenstein and Zhang¹⁴ verified that the carbanions of PMMA could not react with oxirane ring on GMA in THF solutions below -40°C . Our results were in agreement with those of Ruckenstein and Zhang. They reveal that the DPE was an efficient steric hindrance reagent to eliminate any side reactions of the carbonyl groups. As shown in Table II, there were no large fluctuations of molecular weight and distribution at different temperatures (below -60°C). Meanwhile, the extremely low temperature (below -80°C) resulted in a remarkable increase in the viscosity of the solution in this experiment, presumably because of the solubility drop of GMA in toluene. Therefore, it was unfavorable for the further synthesis of polystyrene and PGMA block copolymers with longer GMA segments. Most of our experiments in this study were performed at around -65°C .

Effect of the copolymerization duration on the content of side epoxy groups

Table III shows the effect of different copolymerization times on the content of side epoxy groups on the polystyrene oligomers. With a further increase in the copolymerization time after 30 s, the content of side epoxy groups remained basically unchanged,

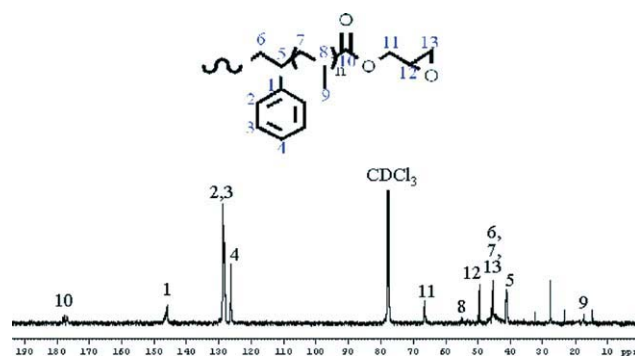
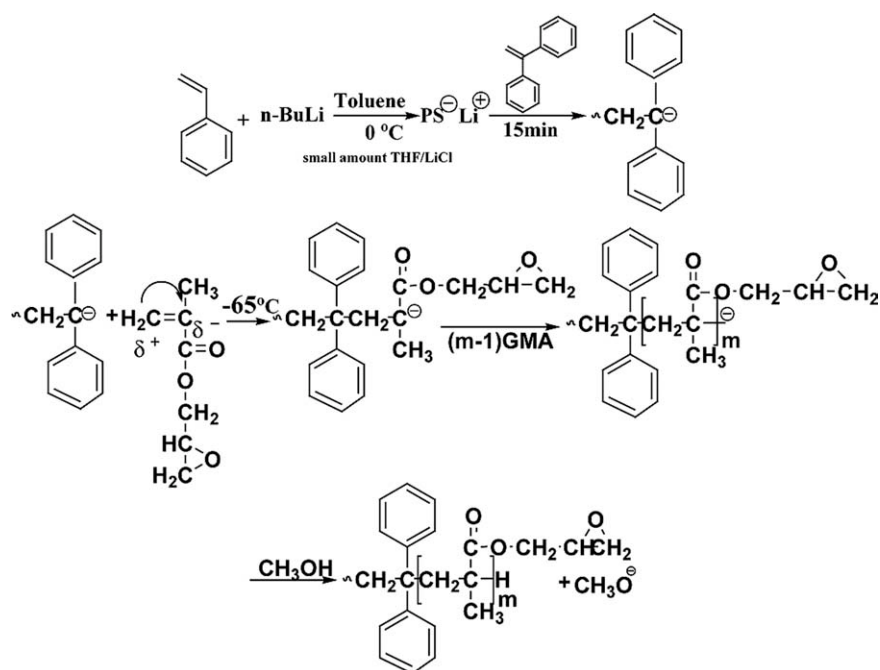


Figure 4 $^{13}\text{C-NMR}$ spectrum of the polystyrene oligomer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 1 Synthesis steps for polystyrene oligomers with several pendent epoxy groups.

even after 10 min. After the reaction was terminated by methanol, no evident unreacted GMA monomer in toluene could be observed by FTIR spectrum. The polydispersity index was approximately 1.1, and the molecular weight was close to the designed value. The copolymerization time (30 s) was long enough to consume all of the monomers without noticeable deactivation of the living sites. The extension of time did not result in side reactions when the copolymerization system was maintained constant copolymerization temperature. Therefore, the copolymerization time could be reduced appropriately to obtain polystyrene oligomers with relatively short (≤ 10) PGMA segments. In this study, most of the copolymer living centers were quenched at 30 s.

Effect of the polystyrene precursor molar mass on the content of side epoxy groups

Table V shows the GPC results of the DPE-end-capped polystyrene precursors quenched by methanol. The results measured by GPC method were very close to theoretical values, and the molecular weight distributions were quite narrow. Clearly, the styrene monomers were polymerized completely, and no chain-transfer reaction was found in toluene at 0–5°C, which was also in agreement with the literature.²¹ The effects of various molar mass of DPE-end-capped polystyrene precursors on the content of side epoxy groups in polystyrene oligomers are shown in Table IV. According to the classic anionic polymerization theory, the DPE-end-capped polystyrene precursors should have had almost the same nucleophilicity, which was only dependent on the

end groups (counterions) instead of the molecular weight of the whole polystyrene chain. The results in the experiments also provided good evidence for it. This was based on the good solubility of polystyrene precursors with relatively small molecule chains in toluene. Otherwise, the curl molecule chains derived from the poor solubility would have caused negative effects on the copolymerization. This factor could possibly be neglected here. This living character of anionic polymerization made it possible to adjust the molecular weight of the polystyrene backbone without affecting the average number of side epoxy groups.

CONCLUSIONS

This study was a rather superficial investigation on the copolymerization of styrene and GMA, and the

TABLE V
Average Molecular Weights and Polydispersity Indices of the Polystyrene Precursors

Sample ^a	M_{th}^b	M_n	M_w	M_w/M_n
S-D-508	2,500	2,679	2,787	1.04
S-D-515	3,500	3,356	3,480	1.04
S-D-516	5,000	4,804	5,029	1.05
S-D-517	7,500	7,244	7,564	1.04
S-D-522	10,000	10,290	10,770	1.05

^a All samples were prepared at 0°C. The concentration of styrene in toluene was 20% (v/v), the [THF]/[*n*-BuLi] ratio was 10 : 1, and the reaction time was 1.0 h.

^b Theoretical value of the molecular weight (calculated from the molar ratio of the monomer to the initiator with the molar mass of DPE neglected).

products reported here had relatively short PGMA blocks. We have provided a new method to synthesize polystyrene oligomers to modify polystyrene. The attempt to use toluene as a solvent was successful. The DPE-end-capped polystyrene precursors were capable of sufficiently initiating the polymerization of GMA in the presence of LiCl under low temperature. During the polymerization, the methacrylic double bonds of GMA were opened, whereas the carbonyl and epoxy groups remained unaffected. The average number of side epoxy groups was close to the theoretical value. The distribution of the molecular weight was close to 1.1. The extension of the copolymerization time and the changing length of the polystyrene chain did not have a significant effect on the epoxy groups of the final products.

References

1. Xie, H.; Sun, W. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1984, 25, 67.
2. Xie, H.; Sun, W. In *Advances in Polymer Synthesis*; Culbertson, B. M.; McGrath, J. E., Eds.; Plenum: New York, 1985; p 461.
3. Mouzali, M.; Lacoste, J.; Abadie, M. J. M. *Eur Polym J* 1989, 25, 491.
4. Jiang, Y.; Liang, E. *Polymer* 1992, 33, 5076.
5. Takenaka, K.; Hirao, A.; Nakahama, S. *Polym Int* 1995, 37, 291.
6. Quirk, R. P.; Zhuo, Q. *Macromolecules* 1997, 30, 1531.
7. Hou, Y. X.; Zhang, H. M. *Gaodeng Xuexiao Huaxue Xuebao* 1995, 16, 974.
8. Hild, G.; Lamps, J. P.; Rempp, P. *Polymer* 1993, 34, 2875.
9. Hild, G.; Lamps, J. P. In *the Wiley Polymer Networks Group Review Series 1*; Nijenhuis, K., Mijs, W. J., Eds.; Wiley: New York, 1998; p 219.
10. Zhang, H.; Hou, Y.; Cheng, C. *Acta Polym Sinica* 1996, 5, 619.
11. Zhang, H.; Ruckenstein, E. *Macromolecules* 1998, 31, 4753.
12. Hild, G.; Lamps, J. P. *Polymer* 1998, 39, 2637.
13. Yoshio, I.; Fujio, T.; Takashi, I.; Kazuyoshi, A. *J Polym Sci Polym Lett Ed* 1967, 5, 29.
14. Ruckenstein, E.; Zhang, H. *J Polym Sci Part A: Polym Chem* 1999, 37, 105.
15. Hild, G.; Lamps, J. P.; Rempp, P. *J Polym Mater* 1997, 14, 99.
16. Hild, G.; Lamps, J. P. *Polymer* 1995, 36, 4841.
17. Gilman, H.; Cartledge, F. K. *J Organomet Chem* 1964, 2, 447.
18. Stenmark, G. A. *Anal Chem* 1957, 29, 1367.
19. Dhal, P. K.; Babu, G. N.; Steigel, A. *Polymer* 1989, 30, 1530.
20. Huang, H.; Zhang, J.; Wei, D.; Hu, F.; Zheng, A.; Xiao, H. *Polym Bull* 2008, 60, 477.
21. Wang, L. S.; Favier, J. C.; Sigwalt, P. *Polym Commun* 1989, 30, 248.