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Studies on the Synthesis and the Reaction Mechanism of Epoxy-Terminated Polystyrene Oligomer

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Summary

The living poly(styryl)lithium was prepared by anionic polymerization with the protection of argon under normal pressure, where styrene, cyclohexane, THF and n-butyllithium were used as monomer, solvent, polar reagent and initiator, respectively. Epoxy-terminated polystyrene oligomers with narrow molecular weight distribution were synthesized by the copolymerization of the end groups of poly(styryl)lithium with glycidyl methacrylate (GMA) at a moderate temperature. The oligomers were characterized using GPC, FT-IR, ^{1}H-NMR, ^{13}C-NMR and Hydrochloric acid-Dioxane Argentimetric method. The effects of GMA dosage, copolymerization duration and temperature on the content of epoxy end group were also studied. The results indicated that the double bond of GMA could polymerize with poly(styryl) carbanion and the content of epoxy end group could be adjusted. It was found that the optimal conditions for the copolymerization were reaction temperature at 10°C and 2 h for copolymerization duration.

Keywords

Polystyrene oligomer, Glycidyl methacrylate, Copolymerization, Epoxy end group

Introduction

Living anionic polymerization is one of the most reliable and useful methods for the synthesis of polystyrene oligomers. When the anionic polymerization is ended, the living poly(styryl)lithium can further react with a compound bearing two functional groups to prepare the polystyrene oligomer with reactive functionality. A number of articles and patents have been published regarding this approach, and the typical end reactive groups are epoxy, vinyl, carboxyl or hydroxy groups etc. [1~7]. It has been well known epoxy groups are relatively stable and can readily react with some compounds, such as alcohol, amine, acid and alkali, leading to the formation of various grafting or block copolymers. In 1992, Xie and Pan [8] reported epoxy-terminated polystyrene which was achieved by the reaction of poly(styryl)lithium with epichlorohydrin. However, the maximum epoxide functionalization yield was only 45%.

Glycidyl methacrylate (GMA) is an interesting monomer, exhibiting a polymerizable methacrylic unsaturation and a reactive epoxy group. For the reaction of the poly(styryl)lithium with GMA, Xiang et al [9] reported the preparation of vinyl-terminated polystyrene via a ring-opening reaction of GMA with poly(styryl) carbanion end-capped with ethylene oxide. However, few publications have dealt with rendering the epoxy groups to polystyrene chains. Only Hild G and Lamps J-P [10] addressed the sequential anionic polymerization of styrene and GMA yielded the diblock and triblock copolymers, but the temperature (-78°C) of synthesis was very severe.

In this paper, epoxy-terminated polystyrene oligomers with narrow molecular weight distribution were prepared via the copolymerization of poly(styryl)lithium with GMA. The key aim of the present work was to verify whether GMA could react selectively with poly(styryl)lithium via its methacrylic double bond under a moderate temperature, thus remaining the pendant epoxy group unaffected. The second aim was to raise the content of epoxy end group for versatile applications.

Experimental

Materials

A.R. styrene (from Shanghai Lingfeng Chemical Reagent Co., Ltd. China) was dried over calcium chloride ($CaCl_2$) for 24 h. It was made free of inhibitor by a first distillation over calcium hydride (CaH_2) under reduced pressure, and vacuum distilled again over sodium wire right prior to use. A.R. cyclohexane (from Shanghai Lingfeng Chemical Reagent Co., Ltd. China) was dried overnight with magnesium sulfate ($MgSO_4$), refluxed with sodium wire with the protection of argon for 10 h, and finally distilled twice. A.R. tetrahydrofuran (THF) (from Shanghai Chemical Reagent Co., Ltd. China) was dried with CaH_2 under reflux for more than 24 h with the protection of argon, distilled, refluxed with sodium wire for 10 h, and finally distilled. GMA (from Dow Chemical Company, 99.4%) was dried over CaH_2 with magnetic stirring for more than 24h and vacuum distilled twice slowly over CaH_2 prior to use, the middle fraction being recovered. n-Butyllithium (n-BuLi) (from Acros, 2.5 M solution in hexane) was diluted with purified hexane and its concentration (1.0 M) was determined by double titration [11].

Synthesis of epoxy-terminated polystyrene oligomer

Anionic polymerization of styrene with n-BuLi as initiator was carried out in cyclohexane at 25°C for 1h with the protection of argon under normal pressure. An oven dried, cyclohexane rinsed flask was prepared first. After 40 ml of cyclohexane, 10 ml of styrene (0.087 mol) and 0.45 ml of THF (the molar ratio of THF to living sites was 3:1) were added into the flask with dry syringes, the flask was cooled to 0°C. A few drops of BuLi solution which were then added slowly to neutralize the remaining protonic impurities in the reaction solution with magnetic stirring. Then the quantitative volume of n-BuLi solution (1.84 mmol) was added at once into the flask under efficient stirring. The solution immediately became red due to the formation poly(styryl) carbanion. The temperature was maintained around 25°C, and the reaction was allowed to last for 1h, followed by the addition of the calculated volume of GMA (the calculated molar ratio of GMA to living sites was 2:1~10:1) under efficient stirring at 10~50°C. After the addition of GMA, the reaction medium turned to faint yellow. The reaction was allowed to last for 0.5~3 h. Then methanol was added to terminate the entire reaction. The resulting solution was poured into ethanol to precipitate the oligomers, and the obtained oligomers was vacuum dried overnight at 50°C.

Characterization

Gel permeation chromatography (GPC)

The absolute molecular weight (based on laser light scattering detector) and molecular weight distribution of the oligomer were determined using a Waters-515 multi-measurement gel permeation chromatography (GPC) (Wyatt Tech. Co. USA). The measurement was carried out using THF as an eluent at 30°C, with a flow rate of 1.0 ml/min and the standard styrene-divinylbenzene copolymers as the gel columns. The concentration of the oligomer's solution was 0.01 g/ml.

Fourier transforms infrared (FT-IR)

FT-IR spectrum of the oligomer was taken with a Nicolet Magna-IR500 infrared spectrophotometer. The deuterated chloroform was used as a solvent to dissolve the oligomer, and then the solution was casted on a piece of KBr salt.

^1H and ^{13}C nuclear magnetic resonance (^1H-NMR and ^{13}C-NMR)

^{1}H-NMR and ^{13}C-NMR spectrum of the oligomer were recorded in the deuterated chloroform using a Bruker AVANCE500 MHZ NMR spectroscope.

Argentimetric method

The content of epoxy end group (it means the number of epoxy end groups / the number of oligomers in this paper) in the oligomer was determined via a known argentimetric method for epoxy group detection [12]. The content of epoxy end group was calculated by means of the following Eq.:

$$\text{The content of epoxy end group} = \frac{(BN - bn) - (SN - sn)}{1000 \bullet W} \bullet M_n$$

Where
B = volume of silver nitrate, ml, used in titrating blank,
S = volume of silver nitrate, ml, used in titrating the oligomer,
N = normality of silver nitrate solution,
b = volume of ammonium thiocyanate, ml, used in titrating blank,
s = volume of ammonium thiocyanate, ml, used in titrating the oligomer,
n = normality of ammonium thiocyanate,
W = the oligomer weight, gram,
M_n= number-average molecular weight of the oligomer.

Results and discussion

GPC

Figure 1 is the double-measurement chromatogram of GPC, in which LS represents the curve of laser light scatting and RI represents the curve of differential refraction, showing the absolute molecular weight and the molecular weight distribution of a polystyrene oligomer (sample PSG-A-3#, see Table 1). The chromatogram consists of a single sharp peak, showing number-average molecular weight (M_n) = 5080, weight-average molecular weight (M_w) = 6590, M_w / M_n = 1.298. The results indicate that the molecular weight distribution is relatively narrow and the determined molecular weight is close to the calculated value, thus demonstrating that the anionic polymerization proceeded in a living manner.

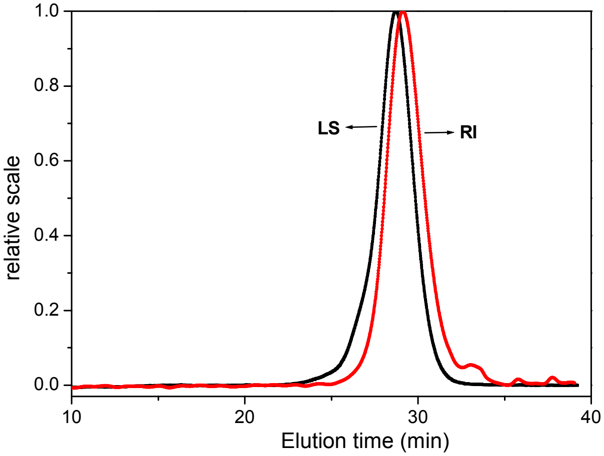


Figure 1. GPC chromatogram of polystyrene oligomer (M_n = 5080, M_w = 6590, M_w / M_n = 1.298, see sample PSG-A-3#, Table 1).

FT-IR

As depicted in FT-IR spectrum of a polystyrene oligomer (see Figure 2 (a), sample PSG-A-4#, see Table 1), the characteristic peaks at 3081,3060,3026,756 and 698 cm^{-1} stand for C-H on benzene ring, and the peaks at 1601, 1492 and 1451 cm^{-1} represent benzene ring. The results confirm the existence of polystyrene. There are not obviously absorbing peaks between 1620 and 1680 cm^{-1}, which suggests that there are not double bonds in the oligomer. In other words, the spectrum shows the polymerization of styrene proceeded completely. On the other hand, it also presumably suggests that the double bond of GMA was involved in the reaction with poly(styryl)lithium. In addition, FT-IR spectrum shows the obvious peak at 1732 cm^{-1} for saturated ester's carbonyl group; while the peak of unsaturated ester's carbonyl group of GMA occurs at 1722 cm^{-1} (see Figure 3). The results indicate that there is no carbonyl group linked with double bond in the oligomer. Therefore, it can be concluded that the absence of the double bond of GMA in the oligomer. Furthermore, the peaks at 907 cm^{-1} and 844 cm^{-1} demonstrate the presence of epoxy group. However, there still is a weak peak at 3433 cm^{-1}, implying that oxirane ring-opening reaction occurred slightly in the course of the copolymerization.

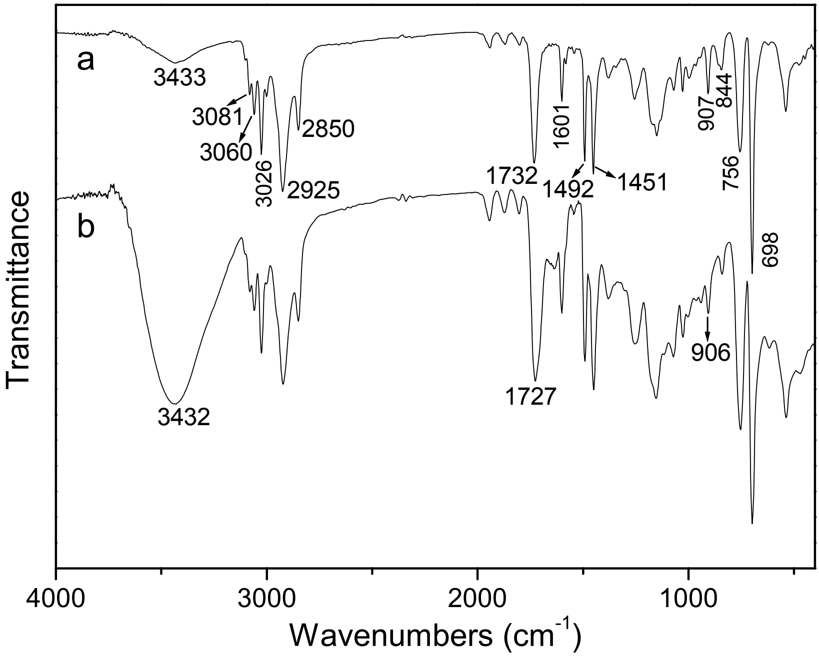


Figure 2. FT-IR spectrum of (a) polystyrene oligomer (see sample PSG-A-4#, Table 1) and (b) polystyrene oligomer reacting with hydrochloric acid.

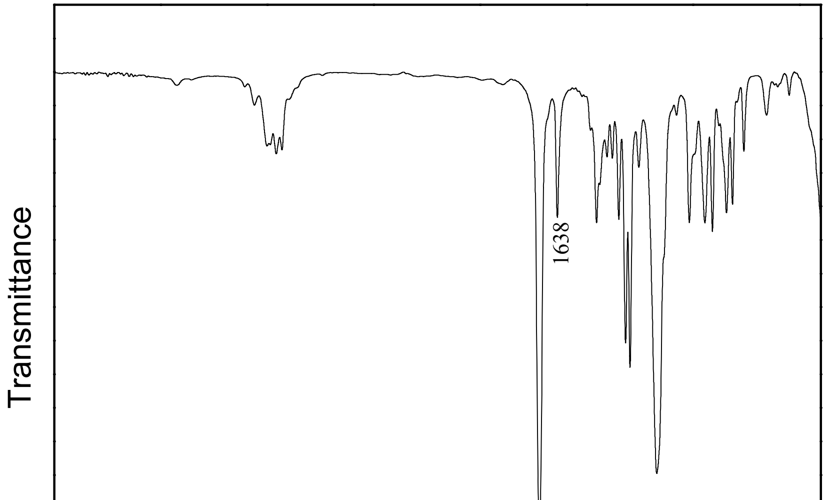


Figure 3. FT-IR spectrum of GMA.

Figure 2 (b) shows the FT-IR spectrum of sample PSG-A-4# reacting with hydrochloric acid. As can be seen, there is a rather intense peak at 3432 cm^{-1} and the peak at 906 cm^{-1} has been obviously weakened, indicating that the hydroxy group was formed by the oxirane ring-opening reaction of epoxy group with hydrochloric acid. This verifies the existence of epoxy group in the oligomer. However, a peak at 906 cm^{-1} for polystyrene is also observed, which overlaps with the peak of epoxy group. As a result, the peak at 906 cm^{-1} can not disappear with the completion of oxirane ring-opening reaction.

^{1}H-NMR

The use of ^{1}H-NMR spectroscopy enables us to determine the composition of polystyrene oligomers. A typical ^{1}H-NMR spectrum of a polystyrene oligomer (sample PSG-B-1#, see Table 2) is shown in Figure 4. The chemical shifts (δ) at 1.43 and 1.59ppm correspond to the protons $–CH_2–$ of monomeric unit of styrene and GMA, and those at 1.87 and 2.05ppm to the proton –CH– of monomeric unit of styrene. The chemical shifts around 6.46 and 7.11ppm stand for the aromatic protons of benzene ring; whereas the shift at 7.24ppm for the protons of $CDCl_3$. In addition, ^{1}H-NMR spectrum shows the chemical shifts at 2.65 and 2.84ppm for the protons $–CH_2–$ and at 3.24ppm for the proton –CH– of epoxy ring. The two peaks at 3.79 and 4.34ppm are assigned to the protons $–CH_2–$ located between the ester and the oxirane function group [10,13,14]. The results also represent the existence of epoxy group. No peaks around 5.6 and 6.8ppm were observed, indicating the absence of the protons corresponding to the methacrylic or unsaturated groups. It can be primarily concluded that the double bond rather than the epoxy group of GMA participated in the reaction with poly(styryl) carbanion.

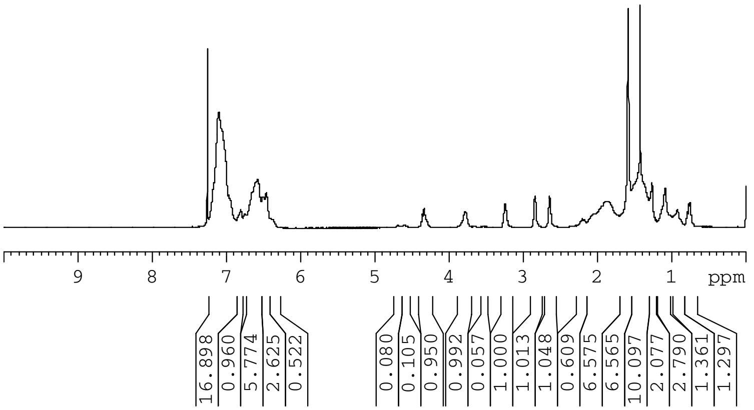
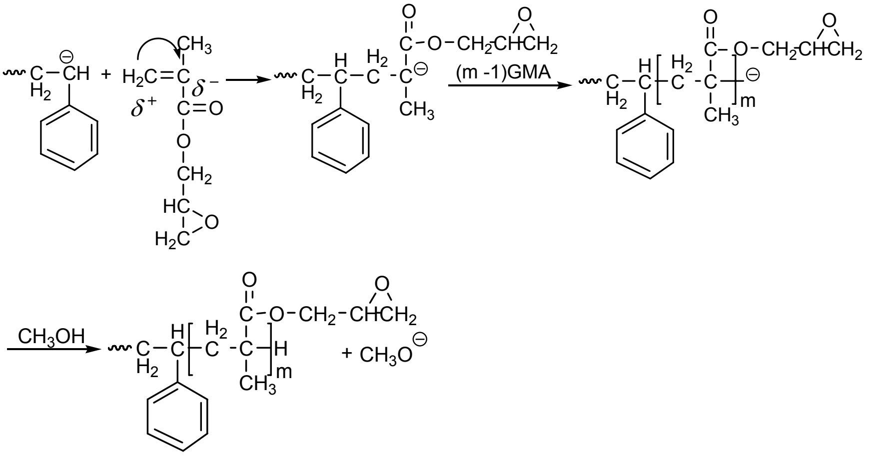


Figure 4. ^{1}H-NMR spectrum of polystyrene oligomer (see sample PSG-B-1#, Table 2).

According to all these analyses addressed above, the possible reaction mechanism is that poly(styryl) carbanion mainly attacks the β carbon atom of the double bond in GMA and opens the double bond to form the α carbanion. Then the α carbanion initiates another GMA monomer to induce the addition polymerization. Finally the polystyrene oligomer having several epoxy groups at the chain end is prepared (see Scheme 1).



Scheme 1

^{13}C-NMR

Further evidence for determining the composition of polystyrene oligomers is provided by ^{13}C-NMR analysis. In the ^{13}C-NMR spectrum (see Figure 5, sample PSG-B-1$^{\#}$, see Table 2), the peak at 41.07ppm corresponds to the carbon –CH– bonded to benzene ring and the multiplet of peaks observed in the range of δ = 43.63~45.82ppm corresponds to the carbons –CH_2– of monomeric unit of styrene and GMA. In addition, the peak at 54.87pp is consistent with the carbon **8** bonded to the ester. The peak at 177.67ppm is assigned to the carbon of carbonyl group. And the peak at 66.59ppm is assigned to the carbon –CH_2– located between the ester and the oxirane function group. ^{1}H-NMR spectrum also shows that the peak at 49.50 is assigned to the carbon –CH– of epoxy ring, but the peak corresponding to the carbon –CH_2–of epoxy ring is located between 43.63 and 45.82ppm, which overlaps with the peaks of the

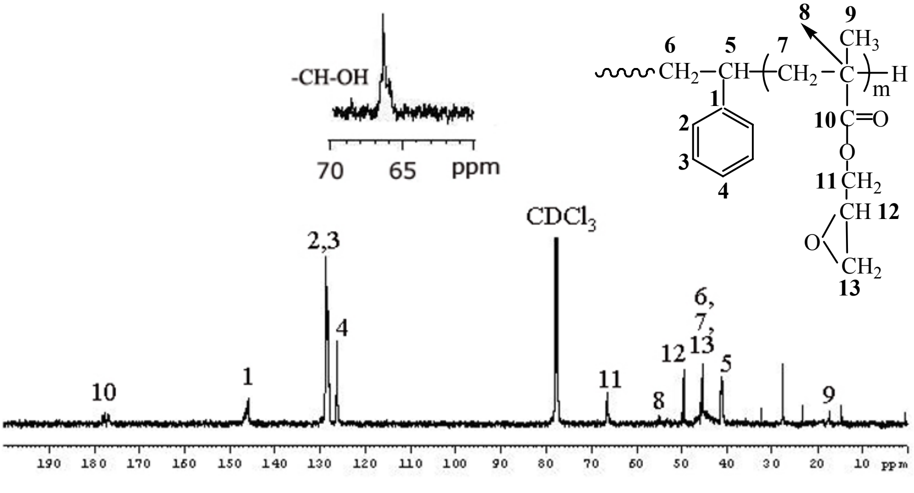


Figure 5. ^{13}C-NMR spectrum of polystyrene oligomer (see sample PSG-B-1$^{\#}$, Table 2).

carbons –CH_2– of monomeric unit of styrene and GMA. However, there still is a very weak peak at 68.65ppm attributed to the carbon –CH–OH, indicating the presence of oxirane ring-opening reaction. It can be concluded that the double bond of GMA polymerized with poly(styryl) carbanion, but oxirane ring-opening reaction occurred slightly in the process of the copolymerization as well.

The effect of GMA dosage on the content of epoxy end group

The polystyrene oligomer can be titrated by Hydrochloric acid-Dioxane Argentimetric method to analyze the content of epoxy end group. The results are shown in Table 1.
It can be found that the content of epoxy end group increases with the increasing of GMA dosage and the determined content of epoxy end group exceeds the expected result (more than 1), indicating that a polystyrene molecule chain is attached more than one epoxy group. This result confirms that the reaction of GMA with poly(styryl)lithium is an addition polymerization achieved by opening the double bond. Therefore, the polystyrene oligomer with several epoxy groups at the chain end can be prepared through Scheme 1. However, when the molar ratio of GMA to n-BuLi reached or exceeded 20:1, crosslinking reaction occured. With respect to FT-IR spectrum of the crosslinked product, it is noteworthy that there is a very intense peak at 3432 cm^{-1} representing the hydroxy group. It is indicated that there was a large number of oxirane ring-opening reactions. According to the above analysis, when the dosage of GMA reaches a certain level, the chain end of polystyrene may has several epoxy groups after the copolymerization. Whereas, the active center of poly(styrene-GMA) carbanion probably also reacts with itself, leading to the crosslinking reaction. However, because the synthesis of styrene and GMA block copolymers were carried out at -78°C (very severe), in the presence of lithium chloride as the additive by Hild G et al [10], the reactivity of the active center reduced, resulting in that oxirane ring-opening reaction was refrained effectively. So the content of epoxy end group was in good accordance with the calculated value and there was no crosslinking reaction with the increasing of GMA dosage.

Table 1. The effect of GMA dosage on the content of epoxy end group

Sample No.	Number-average molecular weight	The calculated molar ratio of GMA to living sites	The content of epoxy end group
PSG-A-1#	4770	2 : 1	1.38
PSG-A-2#	4940	4 : 1	2.46
PSG-A-3#	5080	6 : 1	3.76
PSG-A-4#	5890	10 : 1	6.56
PSG-A-5#	6520	15 : 1	11.49
PSG-A-6#	/	20 : 1	Crosslinking
PSG-A-7#	/	25 : 1	Crosslinking

*Conditions of reaction: concentration of styrenes, 20% (V/V); [THF]/[living sites]= 3:1; copolymerization duration, 2 h; copolymerization temperature, 20°C.

The effect of copolymerization temperature on the content of epoxy end group

The effect of copolymerization temperature on the content of epoxy end group in the polystyrene oligomer is shown in Table 2. It is found that the content of epoxy end group decreases with the increasing of the reaction temperature. Poly(styryl) carbanion tends to react with the vinyl group of GMA selectively, probably due to the high activation energy of epoxy group reacting with poly(styryl) carbanion, thus leaving several epoxy groups unreacted. The reactivity of epoxy group increases with the increasing of temperature, which facilitates oxirane ring-opening reaction. Part of poly(styryl) carbanions probably undergo ring-opening reaction with epoxy groups, resulting in the lowering of the content of epoxy end group in products.

Table 2. The effect of copolymerization temperature on the content of epoxy end group

Sample No.	Number-average molecular weight	End copolymerization temperature (°C)	The content of epoxy end group
PSG-B-1#	5970	10	6.87
PSG-B-2#	5890	20	6.56
PSG-B-3#	5800	30	6.36
PSG-B-4#	6030	50	5.06

*Conditions of reaction: concentration of styrenes, 20% (V/V); [THF]/[living sites]= 3:1; copolymerization duration, 2 h; calculated molar ratio of GMA to living sites, 10:1.

The effect of copolymerization duration on the content of epoxy end group

Table 3 shows the effect of different copolymerization duration on the content of epoxy end group in the polystyrene oligomer. With the increasing of the copolymerization time, the content of epoxy end group increases gradually, which reaches the peak when the reaction time is 2 h, but decreases sharply after 2.5 h. It is indicated that the concentration of the double bond in GMA decreases continually over the copolymerization. However, the number of active centers of poly(styrene-GMA) carbanions does not reduce. It is likely that the poly(styrene-GMA) carbanion attacks the epoxy group to open the ring, then the coupling product is formed, which resulting in the decreasing of the content of epoxy end group. This argument is supported by the ^{1}H-NMR spectrum of sample PSG-C-6# (see Figure 6 and Table 3), in which the peaks of epoxy group in the oligomer have been weakened obviously in comparison with Figure 4.

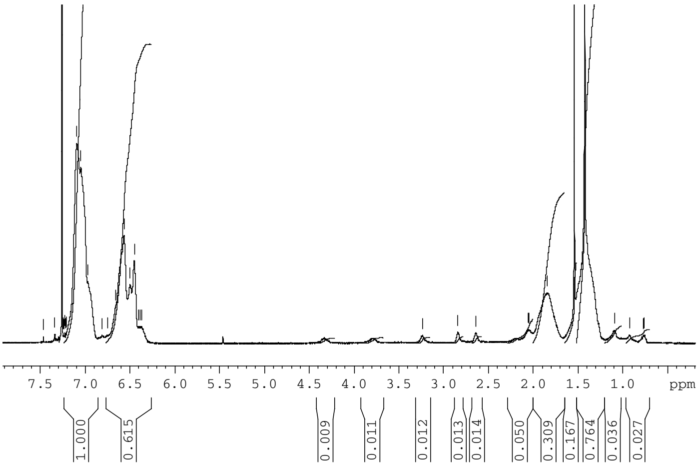


Figure 6. ^{1}H-NMR spectrum of sample PSG-C-6# (see Table 3).

Table 3. The effect of copolymerization duration on the content of epoxy end group

Sample No.	Number-average molecular weight	End copolymerization duration (h)	The content of epoxy end group
PSG-C-1#	5670	0.5	5.94
PSG-C-2#	5760	0.75	6.13
PSG-C-3#	6020	1.0	6.26
PSG-C-4#	5890	2.0	6.56
PSG-C-5#	6240	2.5	4.53
PSG-C-6#	6670	3.0	3.01

*Conditions of reaction: concentration of styrenes, 20% (V/V); [THF]/[living sites]= 3:1; copolymerization temperature, 20°C; calculated molar ratio of GMA to living sites, 10:1.

Conclusions

The living poly(styryl)lithium was formed by anionic polymerization with the protection of argon under normal pressure, where styrene, cyclohexane, THF and n-butyllithium were used as monomer, solvent, polar reagent and initiator, respectively. Epoxy-terminated polystyrene oligomers with narrow molecular weight distribution were synthesized by the copolymerization of the poly(styryl)lithium with glycidyl methacrylate (GMA) at the moderate temperature. In the process of copolymerization, the selective addition polymerization to the vinyl groups in GMA has been performed, thus maintaining the epoxy groups unreacted. The content of epoxy end group is close to the calculated molar ratio of GMA to living sites. When the copolymerization temperature was relatively high or the double bond was consumed, poly(styryl) carbanions tended to react with the epoxy groups, thus lowering the content of epoxy end group or even undergoing the crosslinking reaction. It was found that the optimal copolymerization temperature and the copolymerization duration were 10°C and 2 h, respectively.

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