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Further Studies on the Anionic Copolymerization of Styrene and Glycidyl Methacrylate in Toluene

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Sequential anionic copolymerization of styrene and glycidyl methacrylate (GMA) was performed with the protection of argon under normal pressure, where styrene, GMA, toluene, THF, n-butyllithium and a small amount of lithium chloride (LiCl) were used as first monomer, second monomer, solvent, polar reagent, initiator and additive, respectively. Polystyrene-b-poly(glycidyl methacrylate) diblock copolymers (PS-b-PGMA) with well-defined structure and narrow molecular weight distribution were prepared by the copolymerization reaction of poly(styryl)lithium with GMA under certain temperatures. The copolymers were characterized using gel permeation chromatography (GPC), ¹H-NMR, ¹³C-NMR, thin layer chromatography (TLC) and hydrochloric acid-dioxane argentimetric methods. The effects of additives, copolymerization temperature and THF dosage on the copolymerization were studied. No chain transfer reaction of anionic polymerization of styrene in toluene was observed. Slightly broader molecular weight distribution of PS-b-PGMA was observed with the increase the GMA repeat units. Using THF/toluene blend solvent could reduce the polydispersity index (M_w/M_n) and dissolve the copolymer better than toluene alone. Lower temperature (<-40°C) and LiCl are required to prepare PS-b-PGMA with narrower molecular weight distribution.

Keywords: Block copolymer, glycidyl methacrylate, epoxy group, anionic copolymerization

1 Introduction

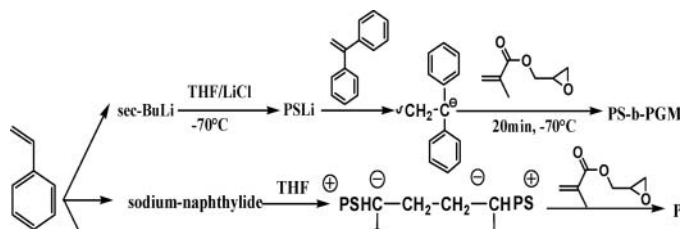
Block copolymers with well-defined structures have been one of the major research focuses in contemporary macromolecular science (1), partly due to their interesting self-assembly behavior in solution. In particular, those reactive block copolymers containing polystyrene building block(s) have found numerous applications as versatile compatibilizers (2) and as back bones for the further reaction to form new copolymers with various architectures (such as graft copolymers, star polymers and polymer brushes) (3–5).

Various methods including chain-end termination and block copolymerization for introducing epoxy groups onto polystyrene macromolecular chain have been investigated (9–17). It is worth noting that the anionic polymerization of GMA is not easy to perform to ensure the epoxy group to be unaffected. In addition, the attack of initiator to carbonyl group or back-bite side reaction should also be

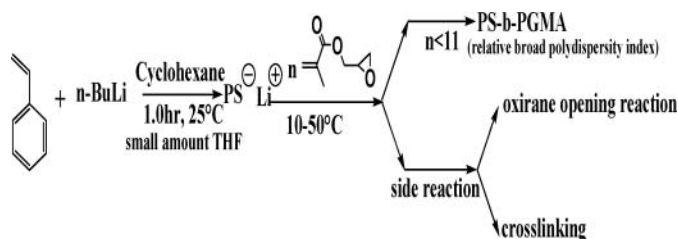
eliminated. In order to stabilize the active center (carbanion species), 1, 1-diphenylethylene (DPE) and LiCl was used as ‘capping agent’ and ligand, respectively. Most of the anionic homopolymerization and copolymerization of GMA are performed in polar solvent such as THF and very low temperature (< -40°C). For example, Hild et al. (13) investigated the sequential anionic copolymerization of styrene and GMA to synthesize the diblock and triblock copolymers (Scheme 1). The molecular weight distributions of prepared di- or tri-block copolymers were relatively broad ($M_w/M_n > 1.1$) (M_n , number average molecular weight, from 13900 to 37000; M_w denotes weight average molecular weight). The whole process was carried out under low temperature (< -55°C) (13). Therefore, in our previous papers (17,18), we tried to divide the whole synthesis process into two separate steps (Schemes 2 and 3), because styrene can be anionically polymerized at higher temperatures (for example, > 50°C). The first attempt to synthesize the styrene and GMA copolymer over ambient temperature by sequential anionic copolymerization was not found to be successful, owing to the inevitable side reaction of oxirane of GMA (17). Even the crosslinking reaction was spotted with increase of GMA repeat units (Scheme 2). The second attempt was to synthesize polystyrene oligomers

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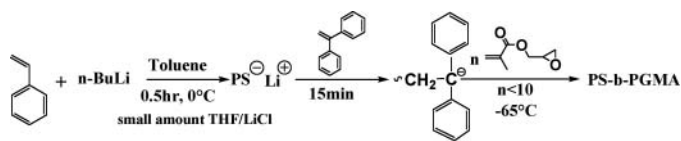
with several epoxy groups on the side chain in toluene under low temperature ($< -65^{\circ}\text{C}$) (18). The polydispersity index of products obtained was very narrow ($M_w/M_n < 1.1$), as long as the number of GMA repeat units of copolymer was confined within 10.



Sch. 1. Schematic illustration of anionic polymerization of PS-b-PGMA and PGMA-b-PS-b-PGMA under very low temperature in THF (13).



Sch. 2. Schematic illustration of an attempt to synthesize PS-b-PGMA via Anionic polymerization under ambient temperature in cyclohexane (17).



Sch. 3. Experimental scheme of synthesizing PS-b-PGMA in this paper.

In this paper, PS-b-PGMA with more GMA repeat units, was synthesized using the same method as in Scheme 3. The effects of solvent and additive (LiCl) on anionic polymerization were also investigated.

2 Experimental

2.1 Materials

2.1.1. Solvents

Toluene (A.R., from Shanghai Lingfeng Chemical Reagent Co., Ltd. China), THF (A.R., from Shanghai Chemical Reagent Co., Ltd. China), methanol (HPLC, from Shanghai Chemical Reagent Co., Ltd. China), absolute ethanol (A.R., from Shanghai Chemical Reagent Co., Ltd. China), Cyclohexane (A.R., from Jiangsu Yangnong

Chemical Reagent Co., Ltd. China) were all processed as in reference (18).

2.1.2. Monomers

Styrene (A.R., from Shanghai Lingfeng Chemical Reagent Co., Ltd. China) was dried over calcium chloride (CaCl_2) for 24 h and distilled twice under reduced pressure over sodium wire immediately prior to use. GMA (from Dow Chemical Company, 99.4%) was stirred in the presence of CaH_2 for 24 h and slowly vacuum distilled twice. The middle fraction was collected and stored in a Schlenk vessel at -20°C , and it was redistilled in the presence of a small amount of diphenyl hexyl lithium (DPHLi) prior to use (11). DPE (99%, from Acros) was distilled twice over sodium wire.

2.1.3. Initiators

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 Gilman double titration (19). 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 .

Lithium chloride (99%, from Acros) was used as received. It was dissolved in THF to form saturated solution.

2.2 Polymerization

2.2.1. Synthesis of polystyrene precursors

Anionic polymerization of styrene was carried out in toluene at 0 – 5°C for 0.5 h with the protection of argon under normal pressure in a glass reactor equipped with a magnetic stirrer. After adding toluene (48 mL), styrene (12 mL) and THF (3.54 mL, the molar ratio of THF to living sites was 10:1) by dry syringes, the glass reactor was cooled to 0°C immediately using an ice-salt bath. The remaining protonic impurities were neutralized by introducing a few drops of diluted n-BuLi solution (0.5 mol/L). The reaction system was faint yellow, indicating the characteristic color of styrene anions. Then, set volume (dependent on the desired molar mass of the polystyrene precursors) of n-BuLi solution (1.0 mol/L) was added immediately into the system under vigorous stirring. The reaction system turned into red color demonstrating the formation of polystyryl carbanions. The reaction was maintained at approximately 0°C to avoid the possible chain transfer reactions in toluene and was allowed to continue for 0.5 h to ensure the complete consumption of styrene. A portion of living polystyrene precursor was sampled to measure molecular weight and polydispersity index using GPC. A 1.2-fold molar excess of DPE was added into polystyrene precursors, instantaneously turning the reaction system into deep red in toluene. The reaction was allowed to continue for 15 min to form DPE-end-capped polystyryllithium.

2.2.2. Synthesis of PS-*b*-PGMA

The calculated volume of GMA (the calculated molar ratio of GMA to living sites ranged from 3:1 to 20:1) was incorporated into DPE-end-capped polystyryllithium all at once, rather than dropwise. The reaction system turned from deep red into faint yellow (characteristic color of methacrylic anions). Viscosity increase was spotted due to the difficulty of stirring. Reaction was finally quenched using degassed methanol, and the product was precipitated in a large excess of ethanol. The copolymers were vacuum dried overnight at 50°C to constant weight. To remove excess DPE, fractionation was performed by the addition of methanol to a 1% solution of polymer in cyclohexane.

2.3 Characterization of polystyrene precursors and PS-*b*-PGMA

2.3.1. Gel permeation chromatography

The molecular weight and molecular weight distribution of the copolymers were determined using a Waters-515 gel permeation chromatography (GPC) (Wyatt Tech. Co. USA). The measurement was carried out at 30°C and at a flow rate of 1.0 mL/min, THF being an eluent. The instrument was calibrated with polystyrene standards (Polymer Laboratories). Samples ($M_n = 2000\text{--}15000$ g/mol) were prepared with a concentration of about 0.01 g/mL in THF.

2.3.2. $^1\text{H-NMR}$ spectroscopy

^1H (500MHz, 500-1000 scans)-NMR spectra of the copolymers were recorded in CDCl_3 using a Bruker AVANCE DRX500 NMR spectrometer. Tetramethylsilane was added to the deuterated solvent as internal standard. Samples were prepared by dissolving 200 mg of polymer in 1.0 mL of the deuterated solvent (deuteron-chloroform, CDCl_3).

2.3.3. $^{13}\text{C-NMR}$ spectroscopy

^{13}C (13000 scans at 125 MHz with $d_1 = 6$ sec)-NMR spectra were also obtained on a Bruker AVANCE DRX500 NMR spectrometer. Samples were prepared by dissolving 200 mg of polymer in 1.0 mL of D_2O .

2.3.4. Thin layer chromatography

Polymers were characterized by thin layer chromatography (TLC). A toluene solution of the copolymer was dropped onto a basic silica TLC plate and was eluted with toluene.

2.3.5. Chemical titration of epoxy groups

The average number of side epoxy groups which means the molar ratio of epoxy groups to the copolymer was obtained via the same argentimetric method for epoxy group detection as described in reference (17).

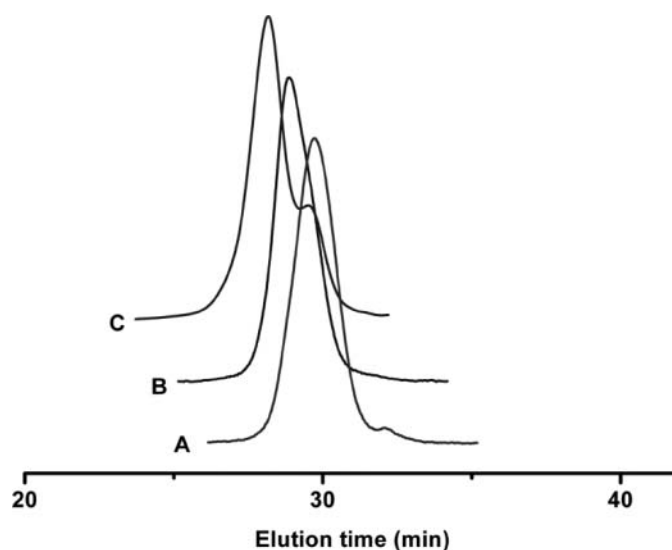


Fig. 1. Typical GPC profiles of PS-*b*-PGMA (A: sample S-G-508; B: sample S-G-805; C: sample S-G-806. See Table 1).

3 Results and Discussion

3.1 Analysis of GPC

The PS-*b*-PGMA was first analyzed by GPC. Some typical GPC traces of the products are shown in Figure 1. The molecular weight distribution of sample S-G-805 (the molar ratio of GMA to living polystyrene precursors is 15:1) is slightly broader than that of sample S-G-508 (the molar ratio of GMA to living polystyrene precursors is 7:1); and even broader for sample S-G-806. The polydispersity index increases slightly as the increment of GMA content on copolymer chain (also see Table 1). Number-average molecular weights of these products were in satisfactory agreement with the theoretical value calculated from the molar ratios of monomer to initiator, and the molecular weight distribution is rather narrow, which demonstrated the anionic polymerization proceeded in a living manner. It is clear that no by-products with high molecular weight were detected, indicating the absence of the side reactions of carbonyl and epoxy groups. However, GPC profile presents bimodal (with a small shoulder peak), implying that the living species did not initiate GMA homogeneously. Moreover, the reaction might be undesirably terminated by impurities introduced by GMA.

3.2 Analysis of $^1\text{H-NMR}$ spectrum and $^{13}\text{C-NMR}$ spectrum

Further characterization was performed with $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$, which can provide structural information about the polymer backbone and side groups of PS-*b*-PGMA. The typical $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of PS-*b*-PGMA (sample S-G-805) are shown in Figures 2 and 3. The two figures are similar to those we reported in

Table 1. The effect of GMA dosage to the content of side epoxy group of PS-b-PGMA

Sample ^a	M_{th}^b	M_n^c	M_w^d	M_w / M_n^e	$\left(\frac{[GMA]}{[n-BuLi]}\right)^f$	$\left(\frac{[GMA]}{[PSLi]}\right)_H^g$	$\left(\frac{[GMA]}{[PSLi]}\right)_T^h$
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	1.13	10:1	10.91	10.72
S-G-805	2500	6586	7973	1.16	15:1	14.20	15.36
S-G-806	7500	9524	11381	1.19	20:1	21.54	18.55

^aAll samples were prepared at -65°C using n-butyllithium in the presence of a small amount of LiCl, concentration of styrene in toluene, 20%(V/V); [THF]/[n-BuLi]=10:1; copolymerization time, 0.5 min.

^bTheoretical values of the molar mass calculated from the mole ratio of styrene monomer to initiator.

^{c,d,e}Experimental values determined by GPC using refractometric detection.

^fThe molar ratio of GMA to n-BuLi.

^gThe average number of GMA repeat units in one copolymer chain calculated from.

^h¹H-NMR.

^hExperimental values of the average number of GMA repeat units in one copolymer chain determined by chemical titration.

reference (18). As we can see in Figure 2, the chemical shifts at 2.65 (e) and 2.84 ppm (d) were attributed to the $-\text{CH}_2-$ protons; and 3.24 ppm (c) to the $-\text{CH}-$ protons of epoxy ring. The two peaks at 3.79 (b) and 4.34 ppm (a) were assigned to the $-\text{CH}_2-$ protons next to the epoxy group (13, 17). Similarly, the peak (around 5.6 and 6.8 ppm) attributed to the carbon double bond proton was not observed, indicating the absence of the protons corresponding to the methacrylic unsaturation. The average numbers of GMA repeat units calculated from ¹H-NMR are listed in the following tables.

As shown in Figure 3, similarly, the characteristic weak signal at $\delta 176.85$ ppm was assigned to carbonyl group on GMA. Carbons of oxirane group have a unique chemical shift in the region between $\delta 44.55\sim 45.82$ ppm and $\delta 49.49$ ppm (20). The chemical shift at $\delta 66.58$ ppm corresponds to the $-\text{CH}_2-$ adjacent to oxirane ring. No by-product of ring-opening reaction of oxirane ring was spotted in ¹³C-NMR spectrum.

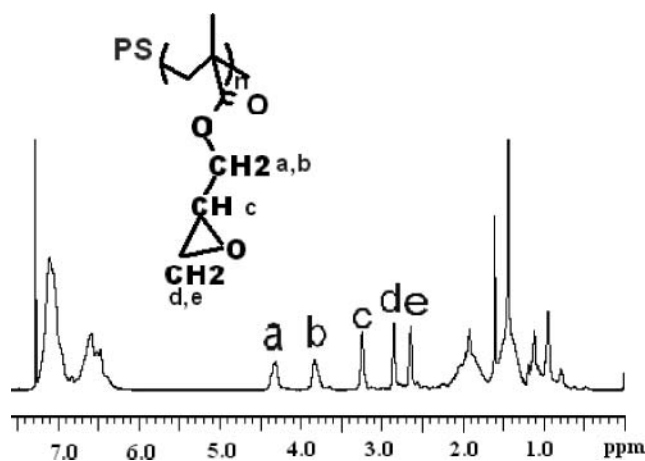


Fig. 2. Typical ¹H-NMR spectrum of PS-b-PGMA (Sample S-G-805. See Table 1).

3.3 Analysis of TLC

TLC picture is shown in Figure 4. The distance of base line up and down is 6 cm. The polystyrene precursor (homopolystyrene) moved from the bottom base line to the top (at a distance of 5.1 cm to the bottom base line), the spot of PS-b-PGMA was found to remain on the base line. There is no absorption effect of silica to nonpolar polystyrene precursor, however there lies in absorptive action of silica to PS-b-PGMA with epoxy and ester groups. This result also indicates that there is no homo-polystyrene side product in PS-b-PGMA.

3.4 Impact Factors Influencing the Process of Polymerization

3.4.1. The effect of chain transfer reaction of toluene as solvent on the synthesis procedure

Anionic polymerization has been regarded as the most useful approach to synthesize tailor-made homopolymers and copolymers. However, solvent (including polar and non-polar solvents) and counter ion might play a key role in the synthesis. Among the non-polar solvents, toluene has been frequently used to synthesize block copolymers; however, toluene also raises the concern related to chain transfer reactions (21). Various studies on the transfer reaction in toluene indicated that toluene may cause secondary reactions (21–24). In contrast, Wang et al. (21) reported that in polymerization of a single batch of monomer over a relatively short period, the chain transfer was insignificant as the transfer constant is probably five orders of magnitude lower than the propagation constant. Longer polymerization time is necessary to reach higher conversion, but also promotes the chain transfer reaction. Therefore, the polymerization of styrene using toluene as solvent should be carefully carried out at a low temperature (e.g., 0°C) and the entire polymerization time need to be deliberately limited to less than 0.5 h. On this basis, the molecular weight

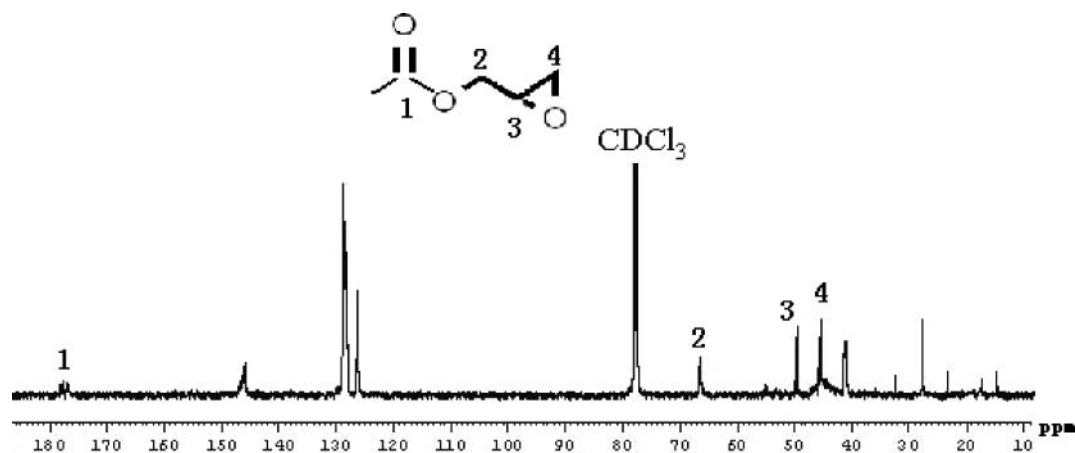


Fig. 3. Typical ^{13}C -NMR spectrum of PS-b-PGMA (Sample S-G-805).

distributions were very narrow ($M_w/M_n < 1.1$), as revealed by GPC (Fig. 5). These demonstrated that the styrene underwent living anionic polymerization in toluene and no obvious transfer reaction occurred during the polymerization.

3.4.2. The effect of GMA dosage

The effect of amount of GMA on the content of side epoxy group, determined by the titration, is shown in Table 1. It was found that the average number of side epoxy group increased with the increasing of GMA dosage and the measured value of epoxy groups were close to the theoretical value. This result also confirmed that the reaction of GMA with DPE end-capped poly(styryl)lithium was an effective

addition polymerization achieved by opening the carbon double bond. It is surprising to see that the molecular weight distribution became broader or appeared to be even bimodal as the increasing of GMA amount. The following two reasons may contribute to the bimodal distribution. On one hand, GMA is extremely difficult to be purified thoroughly, and the impurity in GMA is inevitable. The more GMA was added, the more impurities were incorporated into the system. On the other hand, the GMA homopolymer has poor solubility in toluene, resulting in the sharp increase of viscosity of reaction system. This also gave rise to the heterogeneous initiation and propagation of GMA.

3.4.3. The effect of copolymerization temperature

In our previous work (18), we focused on the reaction of GMA and polystyrene precursors at low temperatures (c.a. -65°C), as well as the effect of reaction temperature on

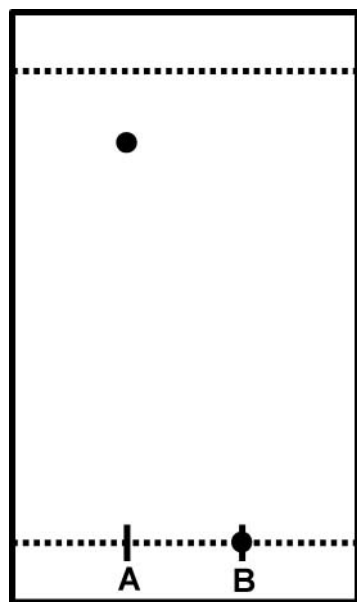


Fig. 4. Thin layer chromatography of polystyrene precursor (A) and PS-b-PGMA diblock copolymer (B); (A, sample S-D-805; B, sample S-G-805).

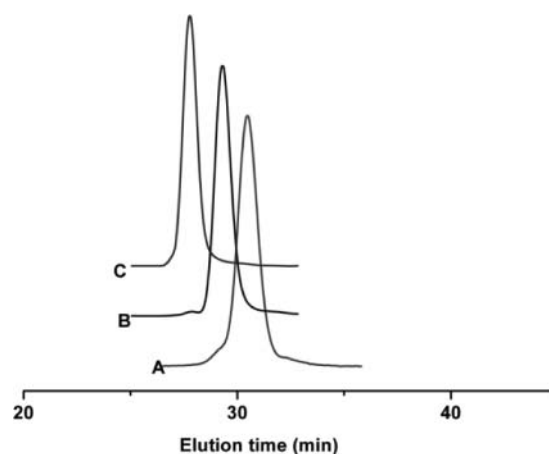


Fig. 5. Typical GPC profiles of PS precursors (A: sample S-D-508, $M_n = 2679$, $M_w = 2787$, $M_w/M_n = 1.04$; B: sample S-D-516, $M_n = 4804$, $M_w = 5029$, $M_w/M_n = 1.05$; C: sample S-D-522, $M_n = 10290$, $M_w = 10770$, $M_w/M_n = 1.05$).

Table 2. The effect of copolymerization temperature to the content of side epoxy group of PS-b-PGMA

Sample ^a	T ^b (°C)	M _n	M _w	M _w /M _n	$\left(\frac{[GMA]}{[PSLi]}\right)_H$	$\left(\frac{[GMA]}{[PSLi]}\right)_T$
S-G-615	-74	3679	4157	1.13	6.89	7.12
S-G-614	-69	3784	4268	1.13	7.63	7.84
S-G-508	-65	3703	4090	1.10	6.85	6.76
S-G-605	-60	3556	4000	1.12	6.02	6.46
S-G-1024	-40	4685	5219	1.11	6.73	6.56
S-G-1022	-20	5040	5811	1.15	6.02	6.14
S-G-1029	0	4964	5882	1.18	5.45	5.61

^aAll samples were prepared in the presence of small amount of LiCl, concentration of styrene in toluene, 20% (V/V); [THF]/[n-BuLi]=10:1; $\left(\frac{[GMA]}{[n-BuLi]}\right) = 7:1$, copolymerization time, 0.5 min; ^bCopolymerization temperature.

the content of epoxy groups. The resulting polymers exhibit narrow molecular weight distribution (less than 1.1). Ring-opening reaction of oxirane and other side reaction did not occur, as detected by GPC, Fourier transform infrared spectroscopy (FT-IR), NMR and chemical titration methods. In order to further understand the influence of reaction temperature, the copolymerization was also performed from -40°C to 0°C. The results including those samples from low temperatures (< -40°C) are tabulated in Table 2. Polydispersity index increases with increment of temperature. Carbanions might attack oxirane ring or carbonyl group at a higher temperature in the same way as we reported in reference (17). In this case, the broad molecular weight distribution is attributed to the side reactions which resulted from the increasing reaction temperature. However, during the experiments, the viscosity of the system was found comparatively increased when the copolymerization temperature was lowered down to approximately -70°C, resulting in broadening of molecular weight distribution. Therefore, the copolymerization temperature should be maintained below -40°C (not lower than -70°C).

3.4.4. The effect of additive (LiCl as ligand)

Table 3 shows the results of PS-b-PGMA synthesized in the absence and presence of LiCl as a ligand. It was found that with the addition of LiCl the molecular weight distribution was narrower than those without the presence of

Table 4. The effect of THF/toluene blend solvent to the copolymerization

Sample ^a	Toluene (mL)	THF ^b (mL)	M _n	M _w	M _w /M _n
S-G-805	48	0	6865	7973	1.16
S-G-905	48	5	5616	6009	1.07
S-G-906	48	10	5580	5989	1.07
S-G-914	48	15	5176	5846	1.13

^aAll samples were prepared using monofunctional "living" polystyrene precursors to react with GMA in the presence of small amount of LiCl $\left(\frac{[GMA]}{[n-BuLi]}\right) = 15:1$, copolymerization time, 0.5 min. Copolymerization temperature was -65°C.

^bThe THF here does not include the THF added with LiCl as solvent and polar reagent.

LiCl. This result was in agreement with those reported by Teyssie et al. (25). LiCl is an effective stabilizer to stabilize the living polystyrene precursors and to avoid the side reaction of epoxy group and carbonyl group, thus leading to desired products. The absence of LiCl tended to create some by-products, particularly when the copolymerization temperature was increased. Hence, the molecular weight distribution became broader accordingly. As LiCl has poor solubility in toluene, a small amount of THF was added into the reaction system to improve the dissolution of LiCl.

3.4.5. The effect of THF addition

It was found that the reaction system became viscous with the increment of GMA dosage. This maybe resulted from the poor solubility of PGMA segment in toluene (9). In essence, di-block copolymer presents properties of both segments. When the number of PGMA segments is much less than that of PS segments in the copolymer chain, it may present the physical properties of PS. Since toluene is a good solvent for PS, the copolymer with a small amount of PGMA segments dissolves well in toluene. However, if the number of PGMA structural units is significantly large compared to styrene repeat units (almost equal or larger than), the physical properties of the diblock copolymer is changed accordingly. This led to the difficulty in dissolving PS-b-PGMA in toluene. The results of using different ratios of THF/toluene blend solvent are shown in Table 4. The polydispersity indices present irregular change. Extra

Table 3. The effect of additive to the content of epoxy group of PS-b-PGMA

Sample ^a	T ^b (°C)	Additive	M _n	M _w	M _w /M _n	$\left(\frac{[GMA]}{[PSLi]}\right)_H$	$\left(\frac{[GMA]}{[PSLi]}\right)_T$
S-G-926	-65	absence	3536	4056	1.15	6.35	6.12
S-G-508	-65	LiCl	3703	4090	1.10	6.85	6.76
S-G-927	-40	absence	3985	4698	1.18	5.85	5.92
S-G-1024	-40	LiCl	4685	5219	1.11	6.73	6.56

^aAll samples were prepared using monofunctional "living" polystyrene precursors to react with GMA in the presence of a small amount of LiCl $\left(\frac{[GMA]}{[n-BuLi]}\right) = 7:1$, copolymerization time, 0.5 min; ^bCopolymerization temperature.

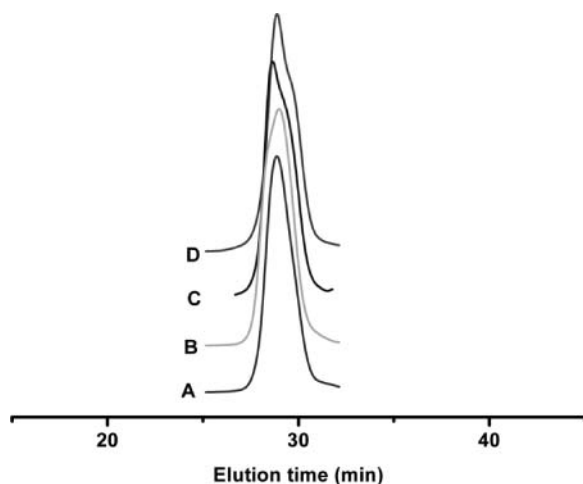


Fig. 6. Comparison of GPC profiles of PS-b-PGMA synthesized by THF/toluene blend solvent. (A: sample S-G-805; B: sample S-G-905; C: sample S-G-906; C: sample S-G-914. See Table 4.)

THF was added after polymerization of styrene. It should be noted that certain impurities would be inevitably introduced into reaction system. These impurities would result in undesired termination of polystyryllithium living species. However, the addition of THF decreased the viscosity of reaction system sharply, which facilitated the stirring or mixing. As a result, Polystyryllithium could interact with GMA monomer intensively, thus initiating the polymerization of GMA homogenously. The relative GPC profiles are shown in Figure 6. The polydispersity index of the last sample (S-G-914) increased and a shoulder peak appeared in GPC profiles might be derived from the undesired termination of polystyryllithium with the increment of THF dosage.

4 Conclusions

In toluene, GMA underwent anionic polymerization on its methacrylic double bond, the epoxy group remaining unaffected during copolymerization in the presence of LiCl, even though the GMA content was increased. No obvious chain transfer reaction was observed during the polymerization of styrene at 0–5°C in toluene. Lowering reaction temperature had minor effect on the synthesis of PS-b-PGMA. The presence of LiCl was essential to prepare PS-b-PGMA with narrower molecular weight distribution even at a lower temperature. In order to prepare well-defined PS-b-PGMA with more GMA repeat units, an appropriate amount of THF should be added to form THF/toluene blend solvent for the copolymerization.

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