Available online at www.sciencedirect.com
ScienceDirect
Polymer 47 (2006) 6575–6580
polymer
www.elsevier.com/locate/polymer

Controlled/living free-radical copolymerization of allyl glycidyl ether with methyl acrylate under ^{60}Co γ-ray irradiation

Qingbo Yu [a,b], Daoben Hua [c], Xueping Ge [a], Ruke Bai [a,*], Mingxu Zhang [b]

[a] Department of Polymer Science and Engineering, University of Science and Technology of China, Anhui 230026, PR China
[b] Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, PR China
[c] School of Chemistry & Chemical Engineering, Suzhou University, Suzhou 215006, PR China

Received 17 January 2006; received in revised form 17 July 2006; accepted 23 July 2006
Available online 9 August 2006

Abstract

An investigation on the copolymerization of allyl glycidyl ether (AGE), an epoxy-functional monomer, with methyl acrylate (MA) was performed in the presence of benzyl 1H-imidazole-1-carbodithioate (BICDT) under ^{60}Co γ-ray irradiation. The polymerizations revealed good characteristics of RAFT process. The content of AGE incorporation into the copolymer increased with higher monomer conversion and higher molar fraction of the AGE in the monomer feed. However, the polymerization could slow down when the fraction of AGE increased in the monomer feed, which might be attributed to the low activity of AGE. Taking advantage of RAFT process, functional block copolymer poly(AGE/MA)-*block*-poly(styrene) was prepared in the presence of poly(styrene) macroRAFT agent, and the copolymer was characterized by ^{1}H NMR spectra and GPC.
© 2006 Published by Elsevier Ltd.

Keywords: Allyl glycidyl ether; γ-Ray irradiation; Living free-radical polymerization

1. Introduction

The copolymerization of nonpolar alkenes with polar vinyl monomers remains an area of great interest, because the combination of the two can greatly enhance the range of currently attainable polymer properties due to the incorporation of functional groups into an otherwise nonpolar material [1]. Pioneering work in this field of nonpolar alkene copolymerization with polar monomers has been carried out in the area of metal insertion polymerization [2–4]. Recently the groups of Klumperman [5–8] and Sen [9–11] reported the controlled copolymerizations of 1-alkene with (meth)acrylate. Klumperman and co-workers had demonstrated that allyl monomer could behave as a comonomer, and chain transfer to allyl monomer could almost be negligible in the ATRP copolymerization of MA and 1-octene [5]. Sen and co-workers reported the synthesis of random copolymers of MA and 1-alkenes resulting in greater than 20% incorporation of the latter into the copolymer [9].

It is a convenient and efficacious method to prepare functional polymers by copolymerization of conventional monomer with functional monomers. During the past years, the use of allyl compounds that possess functional groups such as hydroxyl, epoxy, and ethylenic unsaturated groups was gradually arousing interest [12,13]. These functional groups can be used to prepare block copolymers or elastomeric materials with the appropriate chemistry. Allyl glycidyl ether (AGE) is an interesting and available functional monomer, which has two kinds of reactive functional groups, epoxy and vinyl. Some research works have been published about ring-opening copolymerization of epoxy group to produce a kind of polymer containing allyl ether, which could be used in the cross-linking process [14,15]. On the other hand, AGE was copolymerized with other vinyl monomers via free-radical processes and the reactive epoxy group, which can be transformed into a range of functionalities with subsequent reactions, was introduced into the polymers [16–18].

---

* Corresponding author. Tel.: +86 551 3601699; fax: +86 551 3631760.
E-mail address: bairk@ustc.edu.cn (R. Bai).

0032-3861/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2006.07.049

Solpan and Guven reported the copolymers of AGE and acrylonitrile by bulk polymerization under γ-ray irradiation, and the reactivity ratio had been determined, but it was difficult to control the molecular weight and structures of the polymers [17].

In the past decade, well-defined polymers of vinyl monomers have attracted great attention. There are some living radical polymerization techniques reported to prepare the polymers with controlled molecular weights and structures, such as atom-transfer radical polymerization (ATRP) [19], nitroxide-mediated stable free-radical polymerization (SFRP) [20] and reversible addition-fragmentation chain transfer (RAFT) [21]. However, the number of articles about the polymerization of monomers carrying epoxy groups by living polymerization is limited. The probable reason is that anionic or cationic polymerization is difficult due to the possibility of side reactions caused by the presence of the epoxy group. Until now, there are only a few reports about the polymerization of monomers carrying epoxy groups via ATRP process [22–24].

Although the polymerization was very difficult to control under ^{60}Co γ-ray irradiation and the resultant polymers always had uncontrolled molecular weights and broad molecular weight distributions, recently we achieved controlled/living free-radical polymerizations of vinyl monomers under ^{60}Co γ-ray irradiation in the presence of thiocarbonylthio compounds [25–27], and demonstrated that allyl monomers, such as allyl azide, can be used as functional monomer for the synthesis of azide polymers by controlled/living free-radical copolymerization of allyl azide under γ-ray irradiation [27]. This technique has many advantages, such as being environmentally friendly, occurring at room temperature, involving no metal contamination, without additional initiators, and high penetrating ability.

It is well known that epoxy resins based on glycidyl ethers are used in a variety of applications: as protective coatings, including paints and reinforced plastics, and as adhesives and grouting compounds. We try to develop a promising strategy for the preparation of novel epoxy resins which possess new structures and new properties by living/controlled free-radical copolymerization of allyl glycidyl ether with conventional vinyl monomers. In this paper, an investigation on the copolymerization behavior of AGE with methyl acrylate (MA) is reported in the presence of BICDT under ^{60}Co γ-ray irradiation. The results showed that AGE can be markedly incorporated in the obtained polymers and the copolymerization reveals living characteristics. In addition, a reactive copolymer poly(AGE-*co*-MA)-*block*-poly(styrene) was synthesized in the presence of polystyrene macroRAFT agent. The polymers obtained were characterized by gel permeation chromatography (GPC) and ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra.

2. Experimental

2.1. Materials

MA (Shanghai Chemical Co., China) was dried over CaH_2 overnight, and then distilled under reduced pressure and stored under N_2 at −20 °C prior to use. Styrene (St) was dried over CaH_2 and distilled under vacuum. Tetrahydrofuran (THF) (Shanghai Chemical Co., China) was refluxed with sodium for 24 h and distilled. Benzyl chloride (Shanghai Chemical Co., China) and carbon disulfide (Shanghai Chemical Co., China) were dried over $CaCl_2$ overnight, and distilled. Benzoyl peroxide (BPO) was purified by recrystallization. Benzyl 1H-imidazole-1-carbodithioate (BICDT) [28] and AGE [29] were synthesized according to the related reference. All other chemical agents were used as received.

2.2. Synthesis of poly(AGE-co-MA)

The polymerization was carried out in a sealed tube. The general procedure was as follows. The mixture with various mole ratios (see Table 1) of AGE, MA and BICDT was placed in a 5 mL polymerization tube. After three freeze–evacuate–thaw cycles were performed, the tube was sealed under vacuum. Then it was placed in an insulated room with a ^{60}Co source, and exposed at 60 Gy min^{-1} of dose rate for a prescribed time at room temperature (∼27 °C). After the polymerization, the reaction mixture was dissolved with THF and then precipitated in petroleum ether. The polymer was collected by filtration and dried in a vacuum oven at 35 °C. Conversion (Conv.) was calculated based on Eq. (1):

$$\text{Conv.}(\%) = (W_P - W_{BICDT})/W_m \times 100\% \qquad (1)$$

where W_P, W_{BICDT} and W_m are the weights of the polymer obtained, BICDT and the monomer added, respectively.

The theoretical number-average molecular weight, $M_{n,th}$, was calculated based on Eq. (2):

$$M_{n,th} = W_m/M_{BICDT} \times \text{Conv.}(\%) \qquad (2)$$

where W_m and M_{BICDT} are the weight of monomer added and the moles of BICDT added.

2.3. Synthesis of PSt macroRAFT agent

The mixture of St (6.9641 g, 6.70×10^{-2} mol), BICDT (0.0810 g, 3.46×10^{-4} mol) and BPO (0.0197 g) was placed in a 10 mL polymerization tube. After oxygen was removed, the sealed tube was immersed in a temperature controlled oil bath kept at 90 °C and stirred for 5 h. After the heating was stopped, the reaction mixture was dissolved with THF and then precipitated in methanol. The polymer was collected by filtration and dried in a vacuum oven at 35 °C. The molecular weight and molecular weight distribution of the PSt macroRAFT agent were obtained by GPC ($M_n = 11{,}200$ g mol^{-1}, $M_w/M_n = 1.08$, conversion = 63.3%).

2.4. Synthesis of poly(AGE-co-MA)-b-PS

The polymer was prepared using a similar method to that employed in the preparation of poly(AGE-*co*-MA). In this procedure, PSt ($M_n = 11{,}200$ g mol^{-1}, $M_w/M_n = 1.08$) (0.2560 g, 2.28×10^{-5} mol) was used as the macroRAFT agent, THF as the solvent, MA (0.7175 g, 8.34×10^{-3} mol) and AGE

Table 1
The results of the copolymerizations of AGE and MA under ^{60}Co γ-ray irradiation (60 Gy min^{-1})

Entry[a]	Feed mole ratio of reactants (AGE/MA)	Time (min)	Conversion (%)[b]	Mole fraction of AGE incorporated (%)[c]	$M_{n,th}$[d]	M_n[e]	M_w/M_n[e]
1	0.35	300	30.1	3.1	13,300	16,700	1.17
2	0.35	660	70.4	5.3	30,300	33,000	1.10
3	0.67	300	12.5	5.3	5,300	9,200	1.32
4	0.67	900	37.6	8.2	16,200	19,500	1.25
5	1.00	330	8.0	7.9	–	–	–
6	1.00	1200	23.9	10.4	–	–	–
7	–	300	63.3	–	12,700	11,200	1.08
8	0.35	166	18.5	–	22,200	22,300	1.29
9	0.35	274	31.2	2.4	28,600	28,500	1.27
10	0.35	400	42.7	2.5	34,800	33,600	1.16
11	0.35	660	70.0	3.2	–	–	–

[a] Entries 1–6 show the molecular characteristics of P(AGE/MA) in the presence of BICDT (0.005 g, 2.14×10^{-5} mol) (AGE = 0.2907 g, MA = 0.6299 g for entries 1, 2; AGE = 0.4297 g, MA = 0.4909 g for entries 3, 4; AGE = 0.5200 g, MA = 0.4007 g for entries 5, 6), entry 7 shows that of the PSt macroRAFT agent, entries 8–11 show the molecular characteristics of P(AGE/MA)-*b*-PS block copolymers.

[b] Calculated according to Eq. (1) for entries 1–6 and Eq. (3) for entries 8–11.

[c] Calculated according to Eq. (5) for entries 1–6 and Eq. (6) for entries 8–11, the number of scans for NMR is 64.

[d] Calculated according to Eq. (2) for entries 1–6 and Eq. (4) for entries 8–11.

[e] The data were determined by GPC.

(0.3266 g, 2.86×10^{-3} mol) as the monomer. The sealed tube was irradiated with ^{60}Co γ-ray at 60 Gy min^{-1} for a prescribed time at room temperature (∼27 °C). The procedure for the isolation and purification of block copolymers was the same as that described for the synthesis of PSt macroRAFT agent. Conversion (Conv.) was calculated based on Eq. (3):

$$\text{Conv.}(\%) = W_{\text{P}} - W_{\text{P}'}/W_{\text{m}} \times 100\% \tag{3}$$

where, W_{P}, $W_{\text{P}'}$ and W_{m} are the weights of the polymer obtained, PSt macroRAFT agent and the monomers added, respectively.

The theoretical number-average molecular weight, $M_{\text{n,th}}$, was calculated based on Eq. (4):

$$M_{\text{n,th}} = M_{\text{n,m}} + W_{\text{m}}/[M]_{\text{m}} \times \text{Conv.} \tag{4}$$

where, $M_{\text{n,m}}$, W_{m} and $[M]_{\text{m}}$ are the theoretical number-average molecular weight of the PSt macroRAFT agent, the weight of monomer added and the moles of PSt macroRAFT agent added.

2.5. Characterization of the polymers

The molecular weight and molecular weight distribution were determined by means of a Waters 150C gel permeation chromatography (GPC) equipped with 10^3, 10^4, 10^5 Å columns. THF (1.0 mL min^{-1}) was used as the eluent and the calibration was carried out based on polystyrene standards. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Bruker DMX-300 instrument with $CDCl_3$ as the solvent, and the number of scans is 64 for the polymer sample.

3. Results and discussion

Under conventional radical polymerization conditions, the homopolymerization of allylic monomers is very unlikely, whereas their copolymerization with vinyl monomers are carried out relatively better. We once performed the homopolymerization of AGE under γ-ray irradiation (60 Gy min^{-1}), and a similar result was observed, i.e. almost no polymer was obtained for 20 h. On the other hand, the polymerization of styrene is very slow under γ-ray irradiation [30]. So in this study, the copolymerizations of AGE with MA were carried out under γ-ray irradiation (60 Gy min^{-1}). The results listed in Table 1 indicated that the polymers were formed with narrow polydispersities, and the molecular weight was very close to the theoretical value (entries 1–4, Table 1).

A linear relationship between ln ($[M]_0/[M]$) and polymerization time (Fig. 1) indicates that the polymerization is a first-order reaction with respect to monomer concentration and that the number of radicals remains constant throughout the polymerization. Fig. 2 is a plot of number-average molecular weight against conversion. It is clearly seen that a nearly linear relationship exists between molecular weight and monomer conversion, and the polydispersity is fairly narrow and decreases during the polymerization. All the evidence demonstrates that the polymerization is a ‘‘living’’ free-radical process.

It is worthy to notic that the polymerization slowed down when molar fraction of AGE increased in the monomer feed (entries 1–6, Table 1). For example, in the case of 0.26 molar fraction of AGE, the polymerization could reach 30.1% of conversion within 300 min (entry 1, Table 1); whereas, for 0.50 molar fraction of AGE, it would take 1200 min to get the conversion of 23.9% (entry 6, Table 1). The same phenomena were observed in ATRP and RAFT process by Klumperman, in the copolymerization of butyl acrylate and allyl butyl ether, increasing the fraction of ABE in the monomer feed reduced the overall conversion [8]. The low polymerization rate may be attributed to the inactive end-capping allyl moiety of polymer chain [5]. When the fraction of allylic monomer in the mixture increased, the end-capping of an allylic moiety increased, which led to a decreasing apparent propagation rate.

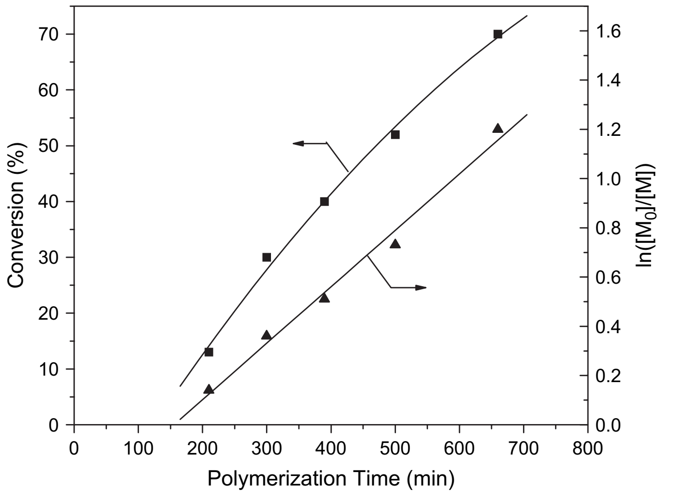

Fig. 1. Conversion and ln ($[M]_0/[M]$) dependence on a function of time for the copolymerization of AGE/MA (0.35 mol/mol) in the presence of BICDT.

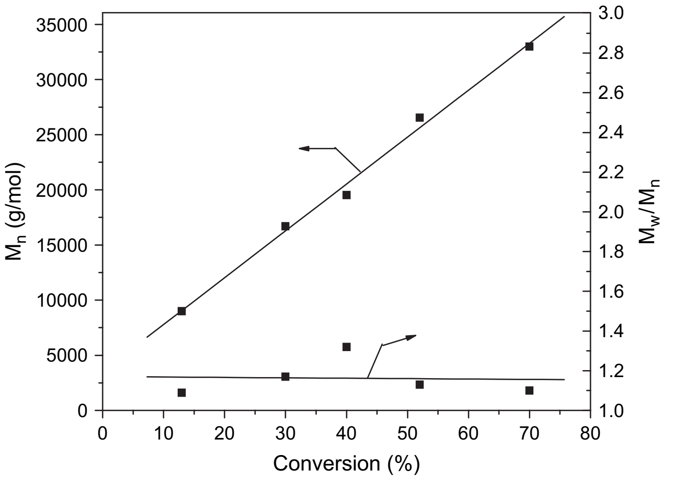

Fig. 2. Molecular weight and molecular weight distribution dependence on conversion for the copolymerization of AGE/MA (0.35 mol/mol) in the presence of BICDT.

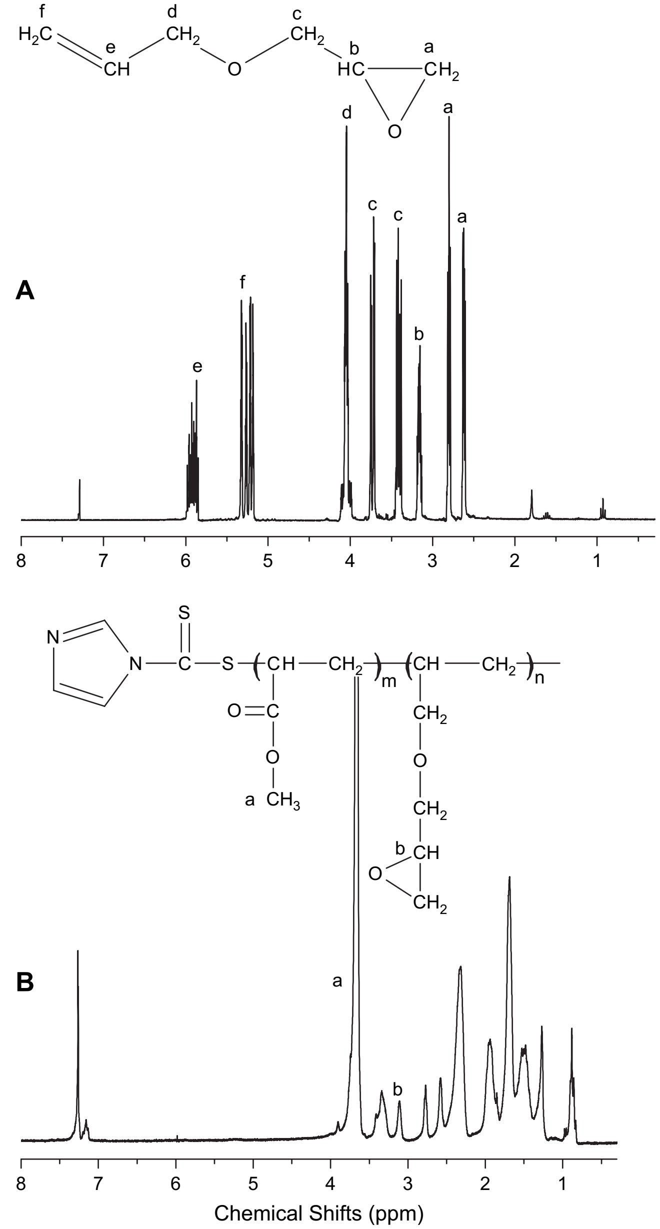

Fig. 3. ^{1}H NMR spectra (300 MHz, $CDCl_3$): (A) AGE monomer, (B) AGE/MA copolymer ($M_n = 9200$ g mol^{-1}, $M_w/M_n = 1.32$).

The polymer structures were characterized by ^{1}H NMR spectra, and a typical spectrum is shown in Fig. 3. In Fig. 3B, the peaks at 3.6–3.8 ppm were ascribed to the methyl protons of the MA units; and by comparing with the spectrum of AGE (Fig. 3A), the signals at 2.5, 2.7, 3.1 ppm revealed that the epoxy ring remained unchanged during the reaction. It should be noticed that the two protons labeled a and c in Fig. 3A had two peaks due to different chemical environments. The molar fraction of incorporation of the AGE into the copolymer, F_{AGE}, could be calculated according to Eq. (5):

$$F_{\text{AGE}} = I_{3.1}/(I_{3.7}/3 + I_{3.1}) \times 100\% \qquad (5)$$

where, $I_{3.7}$ and $I_{3.1}$ are the area of protons of methyl groups of the MA units and the protons of epoxy ring, respectively. The results are listed in Table 1. The level of incorporation of AGE became higher in the copolymer with monomer conversion (entries 1–6, Table 1). In addition, as the molar percent of the AGE was increased in the monomer feed, the fraction of AGE combined in copolymer was higher (entries 1, 4 and 6, Table 1). Since the homopolymerization of AGE is difficult, its incorporation into the copolymer should be attributed to that the addition reaction of AGE-terminated polymeric radicals prefers MA to AGE. Among the similar polar monomer/non-polar monomer systems, the copolymerization of AGE and acrylonitrile had been performed under γ-ray irradiation [17], and the reactivity ratios were found to be 1.86 and 0.21 for acrylonitrile and allyl glycidyl ether, respectively, which further demonstrated the cross-propagation of the two monomers. When the fraction of AGE in the mixture increased with monomer conversion or it was increased in monomer feed, the probability of the AGE incorporation into the polymer chain became higher.

It is well known that polystyrene is one of the most common commercial polymers and is usually introduced into block copolymers to enhance the physical properties of the flexible polymers. We try to demonstrate that styrene block copolymer containing epoxy groups can be synthesized by controlled/living free-radical polymerization under γ-ray irradiation and expect the block copolymer to be a promising precursor for cross-linked polymer materials and functional polymers. Since polymerization of styrene is very slow under γ-ray irradiation [30], PSt macroRAFT agent prepared in the thermal initiation condition was used in the copolymerization of AGE with MA to produce the block copolymers (entry 7, Table 1). The results listed in Table 1 showed that the polymerizations were good controlled/living free-radical processes according to the linear relationship between M_n and conversion and low polydispersities (entries 8–11, Table 1).

GPC curves for the block copolymers are shown in Fig. 4. It could be seen that the polymer peak continuously shifted to higher molecular weights with reaction times, and only sharp and symmetric peaks were obtained. These revealed that all the macroRAFT agents participated in initiating the copolymerization of AGE and MA, i.e. the resultant polymers consisted of poly(AGE-*co*-MA) and PSt.

The structures of the polymers were characterized by ^{1}H NMR spectra, and the typical ^{1}H NMR spectra are shown in Fig. 5. Comparing with PSt macroRAFT agent, besides the protons of phenyl groups of $-C_6H_5-$ (6.4–7.2 ppm), the imidazole was still in the polymer chain (8.4 and 7.6 ppm), and the signals at 2.5, 2.7, 3.1 ppm revealed that the epoxy ring remained unchanged during the reaction. And from the integral area ratio of characteristic peaks, the level of incorporation of the AGE into the copolymer, $F_{AGE,b}$, was calculated according to Eq. (6):

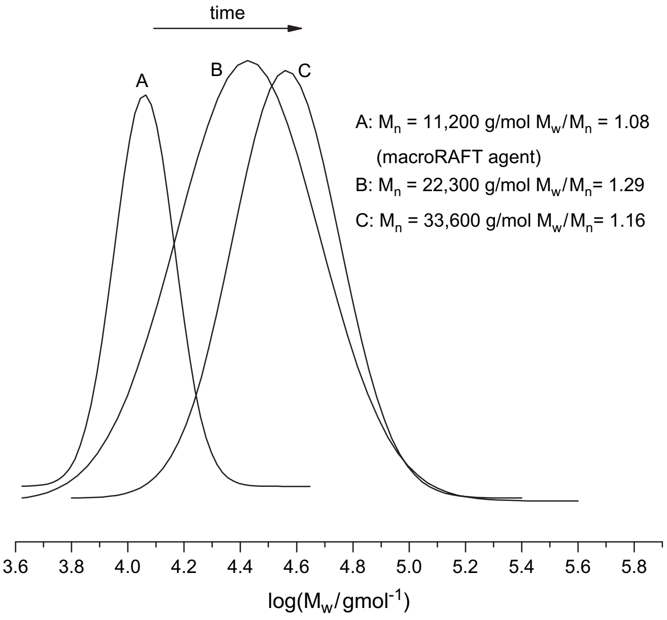

Fig. 4. GPC traces of poly(AGE-*co*-MA)-*b*-PS and PSt macroRAFT agent. (A) Polystyrene macroRAFT agent, (B) poly(AGE-*co*-MA)-*b*-PS (entry 8, Table 1); (C) poly(AGE-*co*-MA)-*b*-PS (entry 10, Table 1).

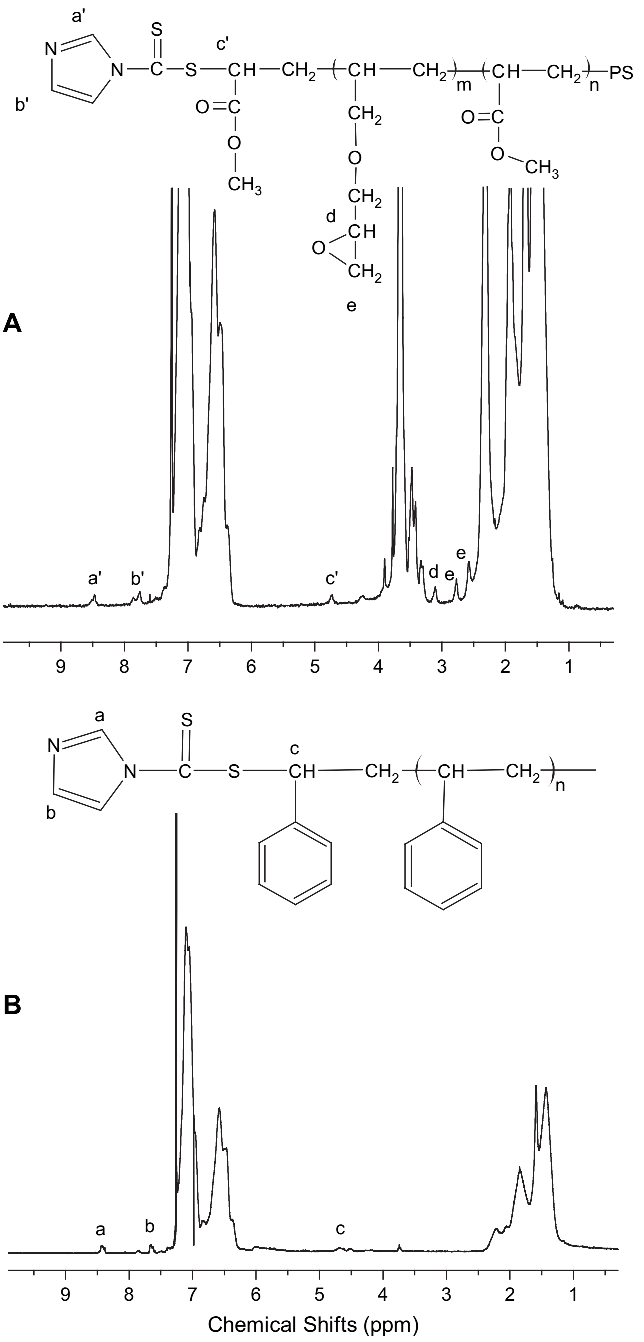

Fig. 5. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of the samples: (A) Poly(AGE-*co*-MA)-*b*-PS (M_n = 15,200 g mol^{-1}, M_w/M_n = 1.11), (B) PSt macroRAFT agent.

$$F_{AGE,b} = I_{3.1}/(I_{7.0}/5 + I_{3.7}/3 + I_{3.1}) \times 100\% \qquad (6)$$

here, $I_{3.7}$, $I_{3.1}$ and $I_{7.0}$ are the area of protons of methyl groups of the MA units, the protons of epoxy ring and phenyl protons, respectively. The results in Table 1 further demonstrated the structure of the block copolymers containing epoxy groups.

4. Conclusions

In conclusion, copolymerization behavior of AGE with MA had been studied under γ-ray irradiation. The polymerization reveals good characteristics of controlled/living free-radical processes, i.e. the molecular weight of the obtained polymer increases linearly with monomer conversion, molecular weight distribution is very narrow, and a linear relationship between $\ln([M]_0/[M])$ and polymerization time exists. The polymer structures were characterized by ^{1}H NMR spectra, and the results indicated that the incorporation of AGE into the copolymer became higher with monomer conversion, and if the molar percent of the AGE was increased in the monomer feed, its incorporation was higher in the copolymer. These phenomena may be associated with the higher probability of the AGE incorporation into the polymer chain due to the relatively higher concentration of AGE in the mixture. However, the polymerization slowed down with molar fraction of AGE increasing in the monomer feed, which might be attributed to the low activity of AGE. The copolymerizations of AGE with MA were also performed to prepare the functional block copolymers in the presence of PSt macroRAFT agent, and the block copolymers were confirmed by ^{1}H NMR spectra. This work developed a promising strategy for the preparation of novel epoxy resins by controlled/living free-radical copolymerizations of AGE with vinyl monomers.

Acknowledgement

We are grateful for the financial support from the National Natural Science Foundation of China under contract No. 20274043.

References

[1] Padwa A. Prog Polym Sci 1989;14:811.
[2] Johnson LK, Killian CM, Brookhart M. J Am Chem Soc 1995;117:6414; Killian CM, Temple DJ, Johnson LK, Brookhart M. J Am Chem Soc 1996;118:11664.
[3] Johnson LK, Mecking S, Brookhart M. J Am Chem Soc 1996;118:267; Mecking S, Johnson LK, Wang L, Brookhart M. J Am Chem Soc 1998;120:888.
[4] Wang C, Friedrich S, Younkin TR, Li RT, Grubbs RH, Bansleben DA, et al. Organometallics 1998;17:3149.
[5] Venkatesh R, Harrisson S, Haddleton DM, Klumperman B. Macromolecules 2004;37:4406.
[6] Venkatesh R, Klumperman B. Macromolecules 2004;37:1226.
[7] Venkatesh R, Staal BBP, Klumperman B. Chem Commun 2004;1554.
[8] Venkatesh R, Vergouwen F, Klumperman B. J Polym Sci Part A Polym Chem 2004;42:3271.
[9] Liu SS, Elyashiv S, Sen A. J Am Chem Soc 2001;123:12738.
[10] Liu SS, Sen A. J Polym Sci Part A Polym Chem 2004;42:6175.
[11] Liu S, Gu B, Rowlands HA, Sen A. Macromolecules 2004;37:7924.
[12] Mark HF, Galyord NG, Bikales NB. Encyclopedia of polymer science and technology, vol. 4. New York: Interscience; 1966. p. 750.
[13] Shigetomi Y, Kojima T, Ono N. J Polym Sci Part A Polym Chem 1990;28:3317.
[14] Tan CS, Juan CC, Kuo TW. Polymer 2004;45:1805.
[15] Lukaszczyk J, Jaszcz K. Reac Funct Polym 2000;43:25.
[16] Jiao SK, Yan H, Xia YZ. Acta Polym Sin 2000;5:623.
[17] Solpan D, Guven O. J Polym Sci Part A Polym Chem 1996;34:833.
[18] Kartal SN, Yoshimura T, Imamura Y. Int Biodeterior Biodegrad 2004;53:111.
[19] Wang JS, Matyjaszewski K. Macromolecules 1995;28:7901.
[20] EP 135280, invs.: Solomon DH, Rizzardo E, Cacioli P Chem Abstr 1985;102:221335.
[21] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al. Macromolecules 1998;31:5559.
[22] Matyjaszewski K, Coca S, Jasieczek CB. Macromol Chem Phys 1997;198:4011.
[23] Krishnan R, Srinivasan SVK. Macromolecules 2003;36:1769.
[24] Cañamero PF, Fuente JL, Madruga EL, Fernández-García M. Macromol Chem Phys 2004;205:2221.
[25] Bai RK, You YZ, Pan CY. Macromol Rapid Commun 2001;22:315.
[26] Bai RK, You YZ, Zhong P, Pan CY. Macromol Chem Phys 2001;202:1970.
[27] Hua DB, Bai W, Xiao JP, Bai RK, Lu WQ, Pan CY. Chem Mater 2005;17:4574.
[28] Wang YQ, Ge ZM, Hou XL, Cheng TM, Li RT. Synthesis 2004;5:675.
[29] Liu HL, Zhang ZL, Zhang JZ. Ind Catal 2003;11:1008.
[30] Hua DB, Zhang JX, Bai RK, Lu WQ, Pan CY. Macromol Chem Phys 2004;205:1125.