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RESEARCH ARTICLE

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Living free-radical copolymerization of allyl glycidyl ether with methyl acrylate

Abstract An investigation of the copolymerization of allyl glycidyl ether (AGE) with methyl acrylate (MA) was performed in the presence of benzyl imidazole-1-carbodithioate (BICDT) on the thermal initiation condition. Results showed that the process has good characteristics of living free radical polymerization, 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 is found. The copolymer structure containing epoxy groups was demonstrated from the 1H nuclear magnetic resonance (1H NMR) spectrum. It was found that the content of AGE in the copolymer increases with the increase in monomer conversion and molar faction of the AGE in the monomer feed. However, the polymerization could slow down when the fraction of AGE increases in the monomer feed. Taking advantage of living polymerization character, functional block copolymers PSt-*b*-P (MA-*co*-AGE) were prepared in the presence of PSt RAFT agent.

Keywords allyl glycidyl ether, living free radical polymerization, benzyl imidazole-1-carbodithioate

1 Introduction

In the past decade, living radical polymerization techniques have attracted great attention. They are reported to prepare the polymers with controlled molecular weights and structures, such as atom-transfer radical polymerization (ATRP) [1], nitnoxide-mediated stable free-radical polymerization (SFRP) [2] and reversible addition-fragmentation chain transfer (RAFT) [3]. One of the most successful systems is RAFT, which has a tolerance to wide variety of functional groups on the monomers and has been applied successfully for the preparation in a well-defined polymerization condition.

During the past years, the use of allyl compounds containing functional groups such as hydroxyl, epoxy and ethylenic unsaturated groups was gradually arousing interest [4–5]. 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 with ring-opening copolymerization of epoxy group to produce the polymers containing allyl ether, which could be used in the cross-linking process [6–7]. On the other hand, AGE was copolymerized with other vinyl monomers via free-radical processes and reactive epoxy group, which can be transformed into a variety of functionalities with subsequent reactions, was introduced into the polymers [8–10]. However, there are a few articles about the polymerization of monomers carrying epoxy groups by living polymerization. The probable reason is that the anionic or cationic polymerization for the monomers carrying epoxy group is difficult due to the side reactions caused by the epoxy group. Until now, there are only a few reports on the polymerization of monomers carrying epoxy group via ATRP process [11–13], such as the homopolymerization of glycidyl methacrylate which was carried out at ambient temperature by ATRP.

It is well known that epoxy resins on the basis of glycidyl ethers have been found in a variety of applications, such as protective coatings, including paints and reinforced plastics, adhesives and grouting materials. Many efforts have been made 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 of

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AGE with methyl acrylate (MA) is reported on the thermal initiation condition using BICDT as initiator. The results show that the process has good characteristics of living free radical polymerization. In addition, a PSt-b-*P*(MA-*co*-AGE) reactive copolymer was synthesized with PSt block as macroRAFT agent.

2 Experimental

2.1 Materials

Styrene (St) and methyl acrylate (MA) were dried over CaH_2 overnight, then distilled under reduced pressure and stored in the refrigerator. Tetrahydrofuran (THF) was refluxed with sodium for 24 h and distilled. Benzoyl peroxide (BPO) was purified by recrystallization. Benzyl 1H-imidazole-1-carbodithioate (BICDT) and allyl glycidyl ether (AGE) were synthesized according to the related references [14,15]. All of the other chemical agents were used as received.

2.2 Polymerization

2.2.1 Synthesis of poly(AGE-co-MA)

The polymerization was carried out in a sealed tube. The general procedure was shown as follows. The mixture composed of various mole ratios (Table 1) of AGE, MA and BICDT was placed in a 5 mL polymerization tube. After three freeze-evacuate-thaw cycles, the tube was sealed under vacuum. Then it was immersed in an oil bath kept at 85°C and stirred. After the polymerization the reaction mixture was dissolved with THF and precipitated in petroleum ether. The polymer then was collected by filtration and dried in a vacuum oven at 40°C.

Table 1 Copolymerizations of AGE and MA

Entry[a]	Feed mole ratio of reactants (AGE/MA)	Time /min	Conversion /%	Mole fraction of AGE incorporation /%	$M_{n,th}$	M_n[b]	M_w/M_n
1	0.36	50	26.8	2.2	12,000	16,200	1.13
2	0.36	80	40.6	5.5	18,200	22,100	1.10
3	0.67	140	38.2	8.4	17,200	21,100	1.09
4	1.00	380	38.5	14.0	17,400	22,800	1.05
5	–	280	48.3	–	9,600	10,300	1.03
6	0.36	540	66	3.6	31,500	32,400	1.14

Notes: [a] Entries 1–4: BICDT = 0.005 g; Entries 1–2: AGE = 0.313 2 g, MA = 0.650 9 g; Entry 3: AGE = 0.451 4 g, MA = 0.510 8 g; Entry 4: AGE = 0.551 6 g, MA = 0.416 1 g, Entry 5: the PSt macroRAFT agent; [b] the data were determined by GPC.

2.2.2 Synthesis of PSt macroRAFT agent

The mixture composed of St (9.008 g, 8.7×10^{-2} mol), BICDT (0.105 1 g, 4.5×10^{-4} mol) and BPO (0.026 0 g) was placed in a 10 mL tube. After oxygen was removed, the sealed tube was immersed in an oil bath kept at 90°C and stirred for 280 min. The reaction mixture was dissolved in THF and then precipitated in methanol. The polymer was collected by filtration and dried in a vacuum oven at 40°C.

2.2.3 Synthesis of PSt-b-P(AGE-co-MA)

The polymer was prepared using a similar method of the preparation of P(AGE-*co*-MA). In this procedure, PSt (0.217 1 g, 2.1×10^{-5} mol) was used as the macroRAFT agent, THF as the solvent, MA (0.702 7 g, 8.17×10^{-3} mol) and AGE (0.302 9 g, 2.66×10^{-3} mol) as the monomer. The procedure for the isolation and purification of block copolymers was the same as that described for the synthesis of PSt macroRAFT agent.

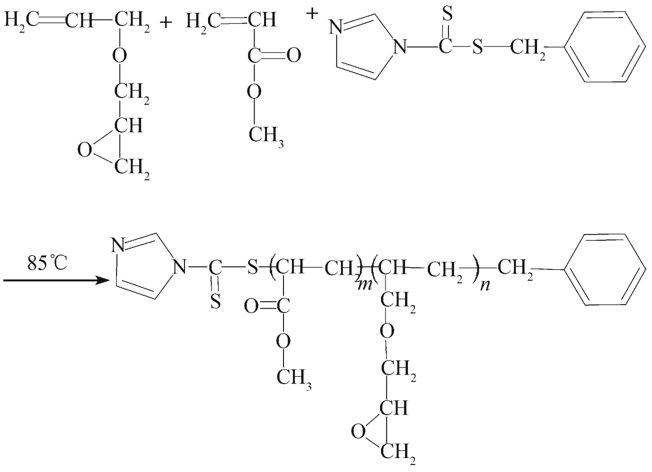
2.3 Characterization of the polymers

The molecular weight and molecular weight distribution were determined by means of gel permeation chromatography (GPC) equipped with 10^3, 10^4, 10^5 Å columns. The THF (1.0 mL min^{-1}) was used as the eluent. ^1H nuclear magnetic resonance (^1H NMR) spectra were obtained on a Bruker DMX-300 instrument with $CDCl_3$ as the solvent.

3 Results and discussion

3.1 Living free-radical copolymerization of AGE with MA

The copolymerization of AGE with MA was performed under the condition of thermal initiation with BICDT as initiator (entries 1–4, Table 1). The reaction is shown as follows



The results listed in Table 1 indicate that the polymers possess narrow polydispersity, and the molecular weight was very close to the theoretical value. Figure 1 is a plot of number-average molecular weight against conversion. It is clear that a nearly linear relationship exists between the molecular weight and the monomer conversion. A linear relationship between ln($[M]_0$/[M]) and polymerization time

(Fig. 2) indicates that the polymerization is a first-order reaction respect to monomer concentration. All of the evidences demonstrate that the polymerization has a “living” free-radical characteristic.

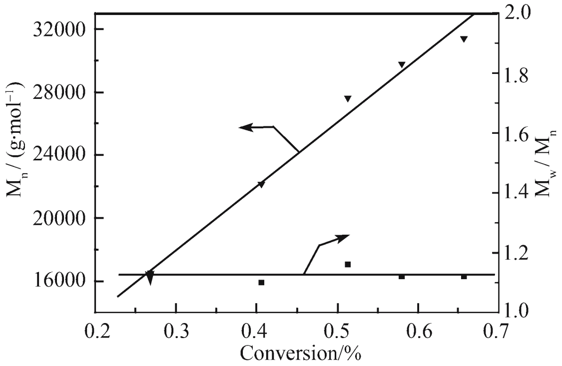


Fig. 1 Molecular weight and molecular weight distribution depending on the conversion of the copolymerization of AGE/MA

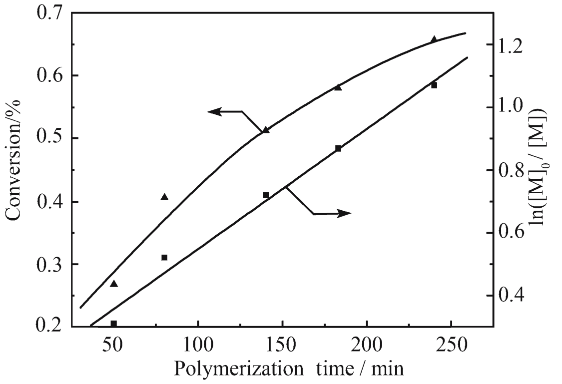


Fig. 2 Conversion and ln($[M]_0$/[M]) depending on the polymerization time for the copolymerization of AGE/MA

3.2 Characterization of the polymers

Under conventional radical polymerization conditions, the homopolymerization of AGE is very unclear, but its copolymerization with MA is relatively better and can be carried out under the normal condition. The copolymer structure of P(AGE-MA) obtained was characterized by ^{1}H NMR and a typical spectrum is shown in Fig. 3. In Fig. 3(b), the peaks at 3.6–3.8 ppm were assigned to the methyl protons of the MA units; and by comparing with the spectrum of AGE (Fig. 3(a)), the signal at 2.5, 2.7, 3.1 ppm reveals that the epoxy ring is unchanged in the copolymers during the polymerization. It should be noticed that the two protons labeled a and c in Fig. 3(a) have two peaks due to the different chemical environments. All of the evidences demonstrate that the copolymerization of AGE with MA has been carried out under the condition of thermal initiation.

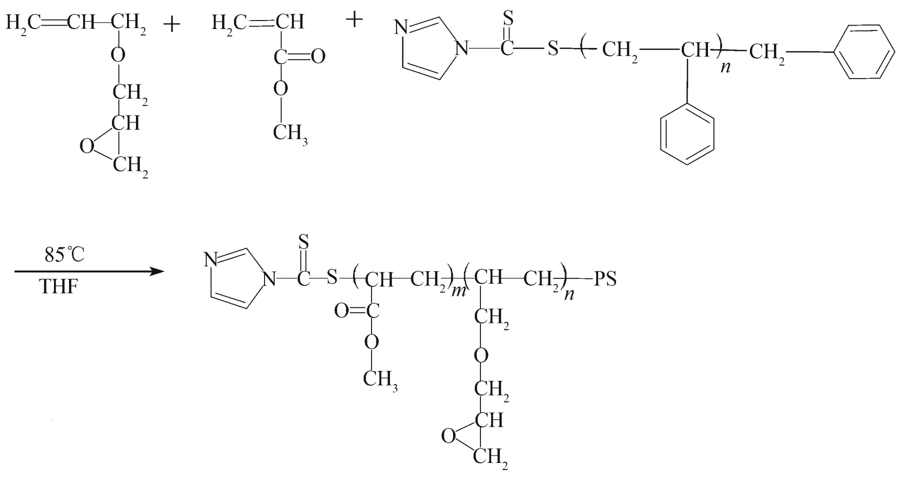
3.3 Level of incorporation of AGE

The level of incorporation of AGE increases in the copolymer with monomer conversion (Entries 1–2, Table 1). In addition, as the molar percentage of the AGE increased in the monomer feed, the fraction of AGE involving in copolymer increases (Entries 2–4, Table 1). Because the homopolymerization of AGE is difficult, its incorporation into the copolymer should be attributed to the addition reaction of AGE-terminated polymeric radical prefers MA to AGE.

In addition, polymerization becomes slow with the fraction of AGE increasing in the monomer feed.

3.4 Synthesis of PSt-*b*-P(AGE-*co*-MA)

It is known that polystyrene is one of the most common commercial polymers and was usually introduced into block copolymers to enhance the physical properties of the flexible polymers. It is demonstrated that styrene block copolymer containing epoxy groups can be synthesized by controlled/living free-radical polymerization, and the block copolymer should be a promising precursor for cross-linking polymer materials. The copolymerization to prepare PSt-*b*-P (AGE-*co*-MA) is shown as follows



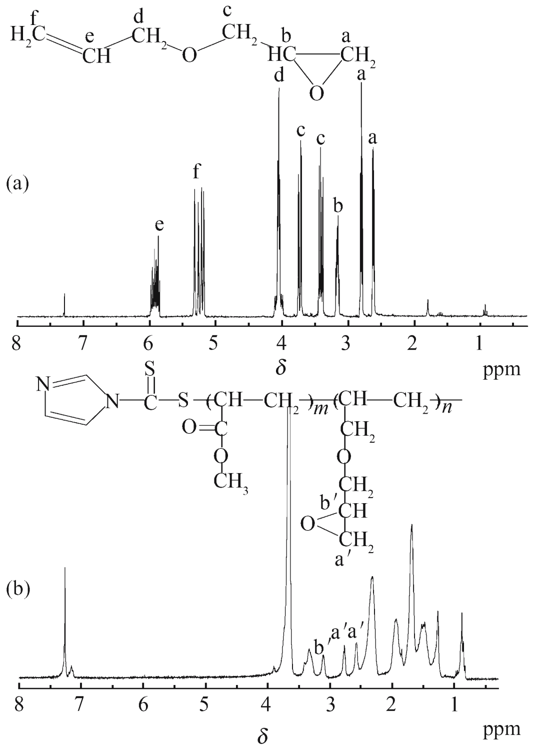


Fig. 3 ^{1}H NMR spectra
(a) AGE monomer; (b) AGE/MA copolymer

PSt macroRAFT agent prepared in the thermal initiation condition was used in the copolymerization of AGE with MA to produce the block copolymers (Entry 5, Table 1). The results listed in Table 1 show that the polymerization is good controlled/living free-radical process because of existing the linear relationship between Mn and conversion as well as low polydispersites (Entry 6, Table 1).

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

The structure of the polymers was characterized by ^{1}H NMR spectra, and the typical ^{1}H NMR spectrum is shown in Fig. 5. The imidazole still exists in the polymer chain (8.4 and 7.6 ppm), and the signals at 2.5, 2.7 and 3.1 ppm reveal that the epoxy ring remains unchange during the reaction.

4 Conclusions

An investigation of the copolymerization of AGE with MA was performed under the condition of thermal initiation. The results showed that the polymerization possesses good characteristics of living free radical polymerization, i.e. the molecular weight of the obtained polymer increases linearly with monomer conversion, the molecular weight distribution is very narrow, and existing a linear relationship between ln([M]$_0$/[M]) and polymerization time. It was found that the content of AGE in the copolymer increases with the increase in monomer conversion and molar faction of the AGE in the monomer feed. However, polymerization becomes slow when the fraction of AGE increases in the monomer feed. Taking advantage of the living polymerization, the functional block copolymers PSt-*b*-P(AGE-*co*-MA) were prepared in the presence of PSt RAFT agent.

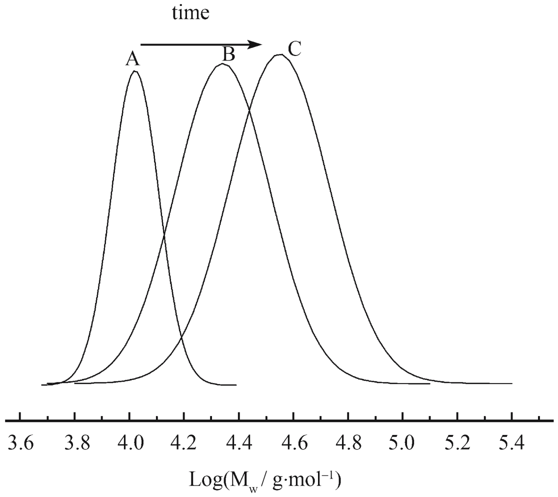


Fig. 4 GPC trances of PSt-*b*-P(AGE-*co*-MA) and PSt macroRAFT agent

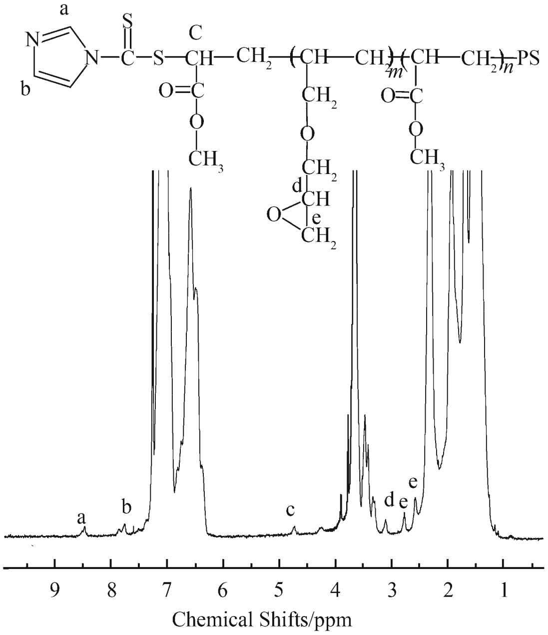


Fig. 5 ^{1}H NMR spectrum of PSt-*b*-P(AGE-*co*-MA)

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