

New Epoxy End-Functional Polystyrene Synthesized by Atom Transfer Radical Polymerization

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A new initiator undecenyl-2-bromopropionate (UBP) was synthesized and it was successfully applied for CuBr-bipyridine (Bipy) mediated ATRP polymerization of styrene (St) at various reaction conditions. The catalyst efficiency was higher at feed ratio of St/UBP = 880 and 400 than ST/UBP = 200. The polymers were obtained with high molecular weight and narrow molecular weight distribution ($M_w/M_n < 1.5$). In the ^1H and ^{13}C NMR spectra of the polystyrene obtained with this catalyst system, the signals assignable to $\text{H}_2\text{C}=\text{CH}$ - group indicate the undecenyl chain-end structure of the polystyrene which confirmed that the ATRP of styrene was initiated by UBP. Finally, the $\text{H}_2\text{C}=\text{HC}$ - group of undecenyl chain end of the polystyrene was converted to epoxy group by oxidation reaction to yield a new epoxy end functional polystyrene. The ^1H NMR spectrum of the polymer confirmed the quantitative conversion of $\text{H}_2\text{C}=\text{CH}$ - to epoxy group.

Key Words: End-functionalization, Epoxy, Polystyrene, Molecular weight, Atom transfer radical polymerization.

INTRODUCTION

End-functional polymers with controlled architecture are currently of great importance in industry and academia and are particularly valued because of their potential applications in surface science and biomedical areas. Because end-groups are retained, the living polymerization processes are particularly suited to the synthesis of end-functional polymers. Thus various living radical methods, including nitroxide-mediated polymerization (NMP)¹ atom transfer radical polymerization (ATRP)² and reversible addition-fragmentation chain transfer (RAFT) with macromonomers³ have all been successfully adapted for this purpose.

The ATRP process allows a large variety of monomers⁴⁻⁸ and the polymer functionality can employ by using a wide range of halogenated initiators and macro-initiators. The synthesis of end-functional polymers by ATRP has been outlined in several reviews^{2,9,10} and continues to be an area of intense interest for synthesis of various end-functional polymers¹¹⁻¹³. The epoxy end group is a very interesting one because it can act as both reactive and polymerizable functional group.

A number of methods based on anionic polymerization for the preparation of well-defined epoxy end-functionalized polymers have been reported by different research groups¹⁴⁻¹⁹. Most of them have synthesized epoxy-end polystyrene by the reactions of epihalohydrin with living polystyryllithium under different conditions. Recently, Matyjaszewski *et al.*²⁰ reported the ATRP polymerization of both styrene and methacrylate using various functionalized initiator including epoxy and allyl group.

Various α -haloesters have been successfully employed for Cu(I)-mediated ATRP⁴. α -Haloesters with various functional groups can easily be prepared through a straight forward esterification reaction of the appropriate acid halides. In this study, a new bromoester bearing undecenyl group was synthesized and it was applied as initiator for synthesis of polystyrenes containing undecenyl group in α -end using Cu(I)-mediated ATRP method. Finally, the undecenyl group of polystyrene obtained was converted to epoxy group *via* chemical modification.

EXPERIMENTAL

Styrene was purchased from Aldrich and was purified by passing through an alumina column to remove stabilizer and then stirred with CaH₂ for 8 h and filtered. Finally it was stored in a Schelk flask at 0 °C under nitrogen prior to use. Copper (I) bromide was purified by recrystallization in methanol and washed with ether. Bipyridine from Fluka, 2-bromopropenyl bromide and 10-undecen-1-ol were purchased from Aldrich and used without further purification. Triethylamine was distilled over CaH₂. All solvents were purified by distillation followed by refluxed with sodium and benzophenone.

Polymerization procedure: Polymerization was carried out in a 50 mL Schelk type reactor equipped with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuBr and bipyridine. Three freeze-pump-thaw cycles were performed and the tubes were sealed under vacuum with rubber septum. A required amount of degassed styrene and initiator were added with syringe. The reactor was placed in an oil bath at the desired temperature and the reaction mixture was stirred for certain time. At timed intervals, the polymerization was stopped by added methanol followed by cooling the reactor into ice-water and the polymer was precipitated in methanol by stirring over night. The polymers obtained were filtered, adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Epoxidation of polymer: 0.5 g of polymer was taken in a 3-necked round-bottomed flask and 70 mL of dry toluene was added. The mixture was heated at 65 °C until the polymer was dissolved completely. Then 0.8 g of *m*-chloroperbenzoic acid in 10 mL of toluene was added. The reaction mixture was stirred for 3.5 h and the reaction was stopped by the addition of methanol. The product was precipitated by the addition of excess methanol. Finally, the product was filtered, washed with methanol and dried under vacuum at 60 °C for 6 h.

Analytical methods: Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by GPC (Waters 150C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. ^1H and ^{13}C NMR spectra of polymers were recorded at room temperature on a Jeol GX 500 spectrometer operated at 125.65 MHz in pulse Fourier Transform mode with chloroform-*d* as solvent. The peak of chloroform in chloroform-*d* (7.26 ppm for ^1H and 74.47 ppm for ^{13}C) was used as internal reference.

Initiator synthesis: Undecen-2-bromopropionate (UBP): A 5.0 g (30 mmol) of 10-undecen-1-ol (**1**) and 5 mL (36 mmol) of triethylamine were dissolved in 80 mL of THF. This solution was cooled in an ice-water bath. To this solution was added drop-wise 3.20 mL (30 mmol) of 2-bromopropenyl bromide (**2**) in 20 mL of THF. The mixture was stirred for 2 h at room temperature (**1** reacted with **2** to yield UBP and HBr; HBr was absorbed by triethylamine). Triethylamine hydrogen bromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolved in CHCl_3 and washed with 50 mL of water 3 times. The aqueous parts were combined and shaken with 50 mL of fresh CHCl_3 . The total CHCl_3 solution was then dried over anhydrous CaCl_2 for overnight. After filtering off the drying agent, CHCl_3 was distilled out under vacuum. A brown liquid was obtained. A further distillation under high vacuum gave a colourless liquid; yield 7.60 g (82 %). ^1H and ^{13}C NMR of this product was analyzed in CDCl_3 (Figs. 2a and 3a).

^1H NMR (CDCl_3): 5.72 ppm (m, 1H, H-b); 4.85 ppm (dd, 2H, H-a); 4.41 ppm (q, 1H, H-l); 4.1 ppm (t, 2H, H-k); 2.00 ppm (q, 2H, H-c); 1.80 ppm (d, 3H, H-m), 1.55 ppm (t, 2H, H-j); 1.2-1.4 ppm (m, 14H, H-d-i).

^{13}C NMR (CDCl_3): 167.46 ppm (C-l); 136.34 ppm (C-b); 111.47 ppm (C-a); 63.30 ppm (C-k); 37.48 ppm (C-m); 31.10 ppm (C-c); 25.71 - 26.73 ppm (C-d-h, j); 23.05 ppm (C-i); 18.97 ppm (C-n).

RESULTS AND DISCUSSION

The initiator undecen-2-bromopropionate (UBP) was synthesized from the reaction between 10-undecene-1-ol and 2-bromopropenyl bromide in the presence of triethylamine. The UBP was characterized by ^1H NMR and ^{13}C NMR analysis. In the ^1H NMR spectrum (Fig. 2a) and ^{13}C NMR spectrum (Fig. 3a) of the UBP, the signals correspond to all protons and carbons of UBP were assigned clearly, which indicated the purity of UBP.

Styrene was polymerized by ATRP method initiated with UBP using copper(I) bromide and bipyridine as a catalyst system under nitrogen atmosphere at 110 °C by changing the ratio of styrene and UBP. The results of the polymerization are listed in Table-1. The ratio of styrene and UBP (St/UBP) significantly affects on the polymerization. The conversion was almost same at the ratio of St/UBP = 800 and 400) and it was about half at ratio St/UBP = 200. The molecular weight of the polymer was measured by GPC and the GPC curves of the polymers were displayed

in Fig. 1. The polymers obtained with this catalyst system showed high molecular weight (M_n) and narrow molecular weight distribution ($M_w/M_n < 1.5$). The M_n value of the polymers obtained was decreased with decreasing St/UBP ratio, whereas the M_w/M_n was almost constant. The theoretical M_n values were comparable to the experimental M_n values of the polymers.

TABLE-1
EFFECT OF THE RATIO OF STYRENE/UBP ON THE POLYMERIZATION OF
STYRENE WITH CuBr/BIPYRIDINE (Bipy)*

Entry	St/UBP (mmol/mmol)	Conversion (%)	M_n (theo)	M_n (gpc)**	M_w/M_n (gpc)**
1	800	43	19025	18864	1.47
2	400	21	9695	9759	1.50
3	200	13	3120	4863	1.50

*Polymerization conditions; CuBr = 0.08 mmol, BiPy = 0.24 mmol, temperature = 110 °C, time = 2 h. **Number average molecular weight and molecular weight distribution were measured by GPC analysis using polystyrene standard.

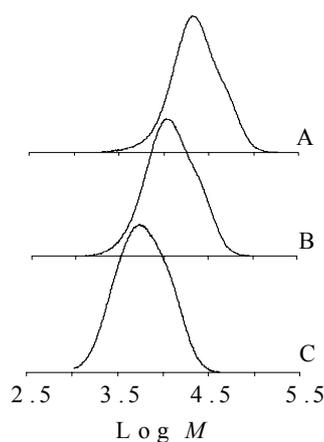


Fig. 1. GPC curves of the polystyrene obtained from different ratio of styrene/UBP (A) 800, (B) 400 and (C) 200 ratio

The structure of the polystyrene obtained was characterized by ^1H and ^{13}C NMR analysis of the polymer and comparison with those of UBP initiator. The ^1H NMR spectra of polystyrene and UBP were compared in Fig. 2. In the ^1H NMR spectrum of polystyrene (Fig. 2B), the signals observed at 5.6 and 6.3 ppm assignable to $\text{H}_2\text{C}=\text{CH}$ - protons (H-a and H-b), at 4.7 ppm for CH proton of α to Br (H-r) and at 4.0 ppm for H-l and H-k. These assignments indicate the presence of undecenyl group in the polymer. Two broad signals observed at 7.28 ppm assignable to aromatic protons H-t and H-u (*meta*- and *para*-position) and at 6.75 ppm for *ortho*-proton H-s of styrene unit. The signals observed at 1.50 and 2.00 ppm assignable to CH_2 and CH protons (H-o and H-p) of main chain of polystyrene.

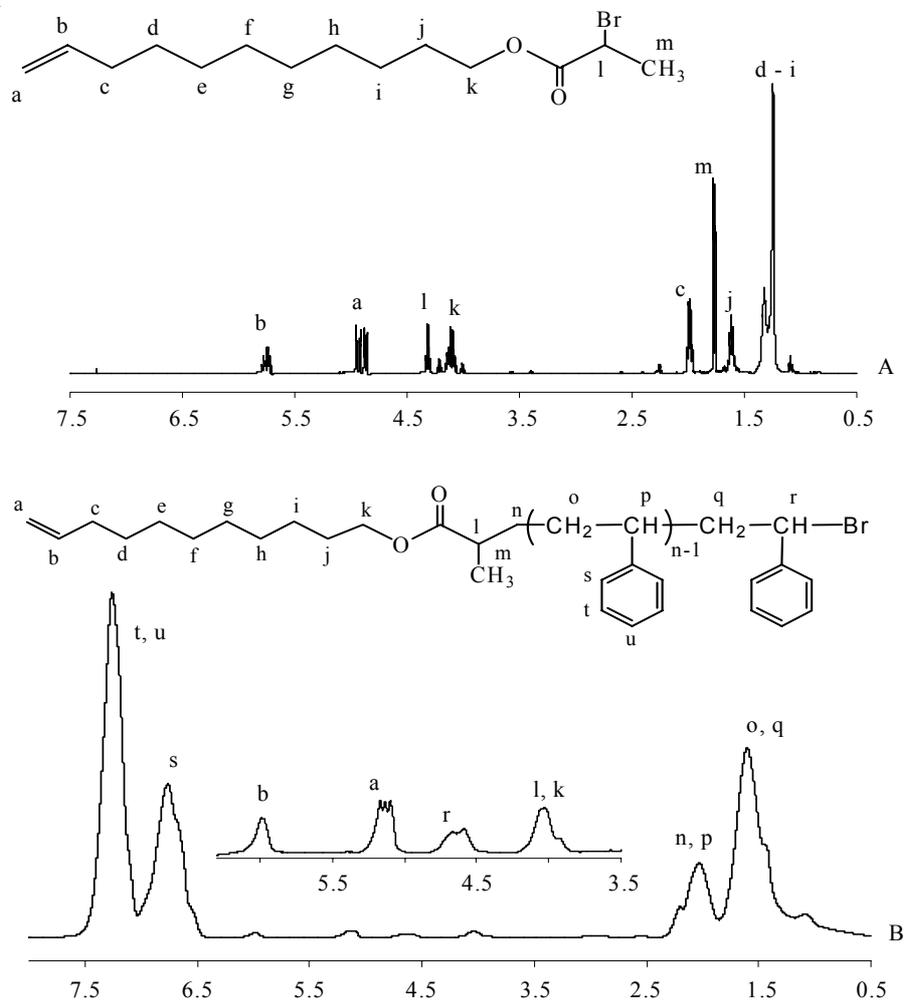


Fig. 2. ¹H NMR spectra of UBP (A) and polystyrene (B) obtained by using UBP as initiator

The ¹³C NMR spectrum of polystyrene was compared with that of UBP initiator in the Fig. 3. The signals at 136.34 and 111.47 ppm assignable to H₂C=CH- carbons and the signals at 22-31 ppm assignable to saturated carbons of undecenyl group clearly indicate the undecenyl chain-end structure of the polystyrene. The signals assignable to carbon atoms of styrene unit were also observed in the ¹³C NMR spectrum of the polymer as follows: at 143, 127, 126 ppm for aromatic carbons labeled as t, u, v and w; at 50 ppm for CH₂ carbon β to Br labeled as r; at 43 ppm CH carbon α to Br labeled as s; and at 38-42 ppm for CH₂ and CH carbons of main chain of polystyrene labeled as p and q. These results clearly indicate the undecenyl chain end of polystyrene obtained with ATRP method using CuBr/Bipy/UBP catalyst system.

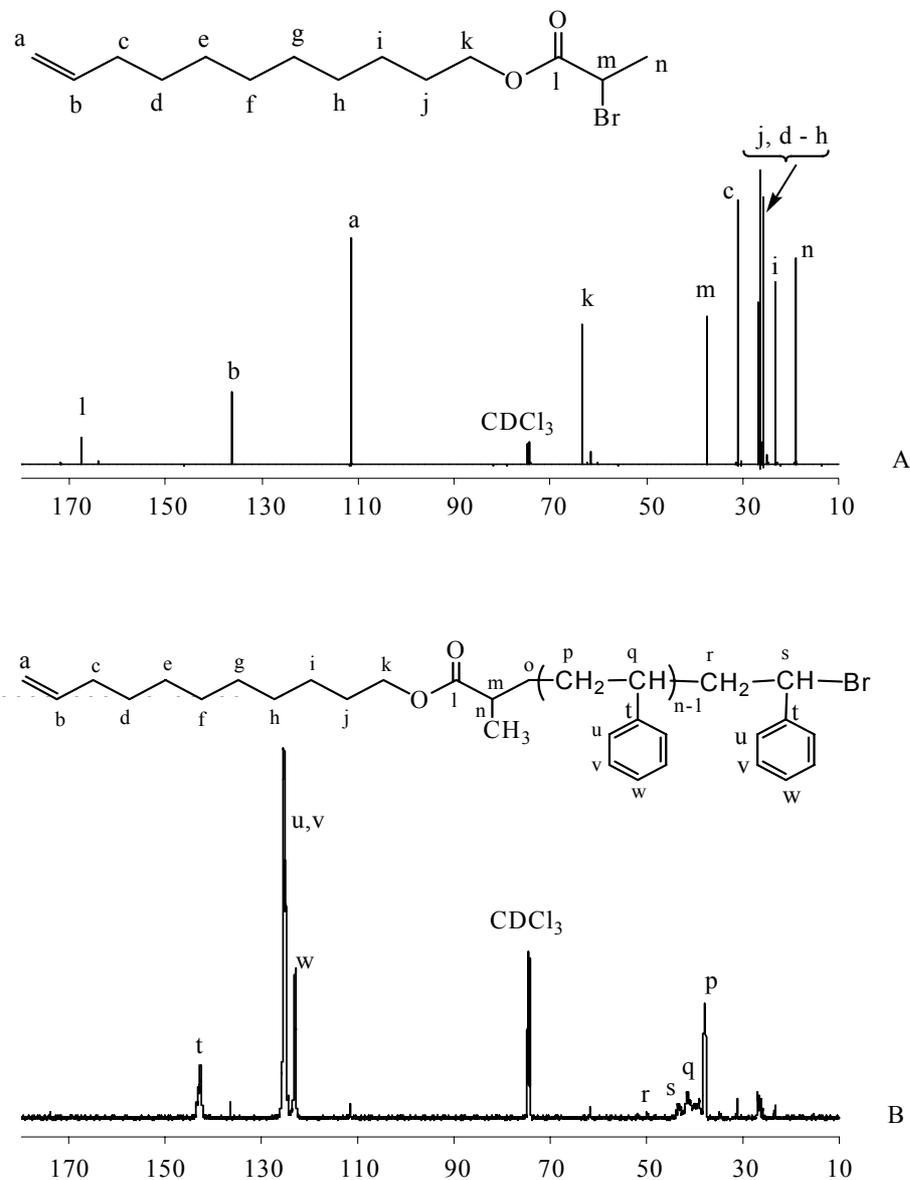


Fig. 3. ^{13}C NMR spectra of UBPA (A) and polystyrene (B) obtained by using UBPA as initiator.

Epoxydation of the polystyrene obtained: The epoxydation of the vinyl group at the chain end of the polystyrene obtained with UBPA initiator was carried out by oxidation with *m*-chloroperbenzoic acid at 65 °C in toluene for 4 h. The quantitative conversion of $\text{H}_2\text{C}=\text{CH}-$ group to epoxy group was confirmed by the ^1H NMR analysis of the product.

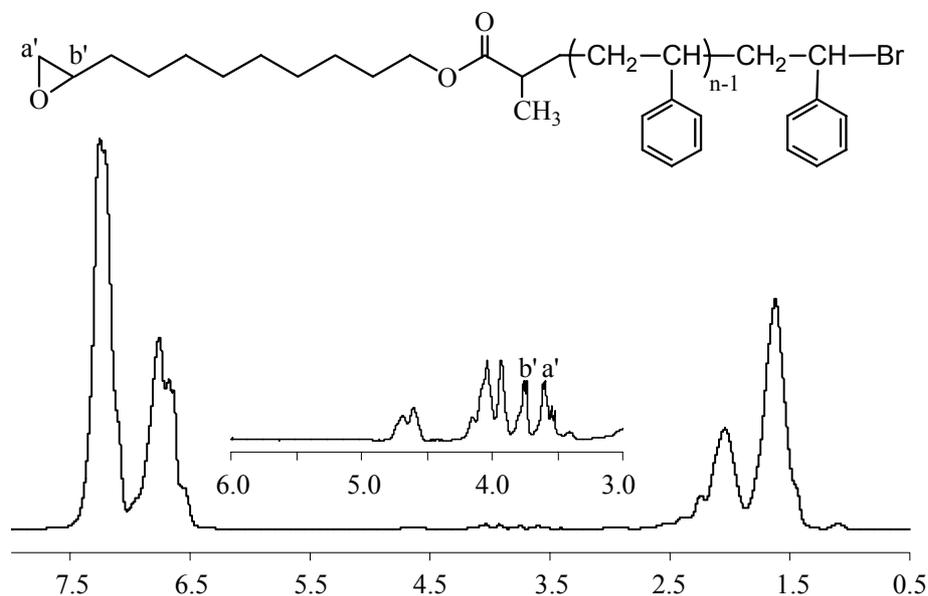


Fig. 4. ^1H NMR spectrum of the epoxy-functional polystyrene

The ^1H NMR spectrum of the polystyrene after epoxidation is displayed in Fig. 4. Complete epoxidation was rationalized from the disappearance of the peak of $\text{H}_2\text{C}=\text{CH}-$ protons at 4.98 and 5.22 ppm in the spectrum of the polystyrene after epoxidation. On the other hand, two broad peaks at 3.62 and 3.77 ppm assignable to epoxy protons ($-\text{CH}-\text{O}-\text{CH}_2-$) were appeared in the ^1H NMR spectrum of the epoxidized polymer.

Conclusion

Undecenyl-2-bromopropionate (UBP) was synthesized and the structure of UBP was characterized by ^1H and ^{13}C NMR analysis. The UBP as initiator was successfully applied for Cu(I)-bipyridine mediated ATRP polymerization of styrene. The polymers obtained with this system showed high molecular weight and narrow molecular weight distribution ($M_w/M_n < 1.5$). Undecenyl chain-end structure of the polystyrene was confirmed by the ^1H and ^{13}C NMR spectra of the polymer. The conversion of $\text{H}_2\text{C}=\text{CH}-$ group of undecenyl chain-end to epoxy group to yield a new epoxy end-functional polystyrene.

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