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The synthesis of ABA block copolymers by means of 'living'/controlled radical polymerization using hydroxyl-terminated oligomers as precursor

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Abstract

ABA block copolymers with well-defined structure were synthesized by the combination of the end-group transformation of prefabricated hydroxyl-terminated oligomers and atom transfer radical polymerization (ATRP). The hydroxyl-terminated oligomers, such as polyether diol, polyester diol and hydroxyl-terminated polybutadiene, were reacted with chloroacetyl chloride to form α,ω–bichloroacetyl oligomers (P–Cl). After the P–Cl was characterized by IR and chlorine content analysis, it was used as macro-intiator in the bulk polymerization of styrene in the presence of CuCl/bpy, which led to a series of ABA block copolymers. The formation of block copolymers was proved by ^{1}H-NMR. The molecular weight of the block copolymers could be designed up to 10^5 according to the consumed monomer and the amount of feeding P–Cl. The kinetic study showed that the relationship between the logarithm of monomer concentration and the reaction time was linear, and an induction period was observed. It suggested that the initiation is slow and the concentration of active species was constant after initiation. Moreover, the experimental molecular weight increased linearly with the monomer conversion; simultaneously, the molecular weight distribution (MWD) of the block copolymer was close to the MWD of the macro-initiator (P–Cl). The results demonstrate the polymerization is a 'living'/controlled process. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Block copolymers usually have integrative mechanic properties because of the microphase separation, so the synthesis of block copolymer is important not only in commercial end usage but also in scientific research [1].

Although many methods have been used to produce block copolymers, living polymerization is the only way to synthesize block copolymer with well-defined structure [2]. It has been proved that anionic polymerization is an effective method to produce such block copolymers. However, the scope of the monomer used for ionic polymerization is limited, while the conditions of anionic polymerization are rigorous. This restricts the application of this method [1].

Recently, the polymerization of vinyl monomers in the presence of alkyl halides (R—X)/CuX/bpy,X = Cl or Br, was reported by Matyjaszewski's group as atom transfer radical polymerization (ATRP) [3]. The polymerization has been proved to proceed with a 'living'

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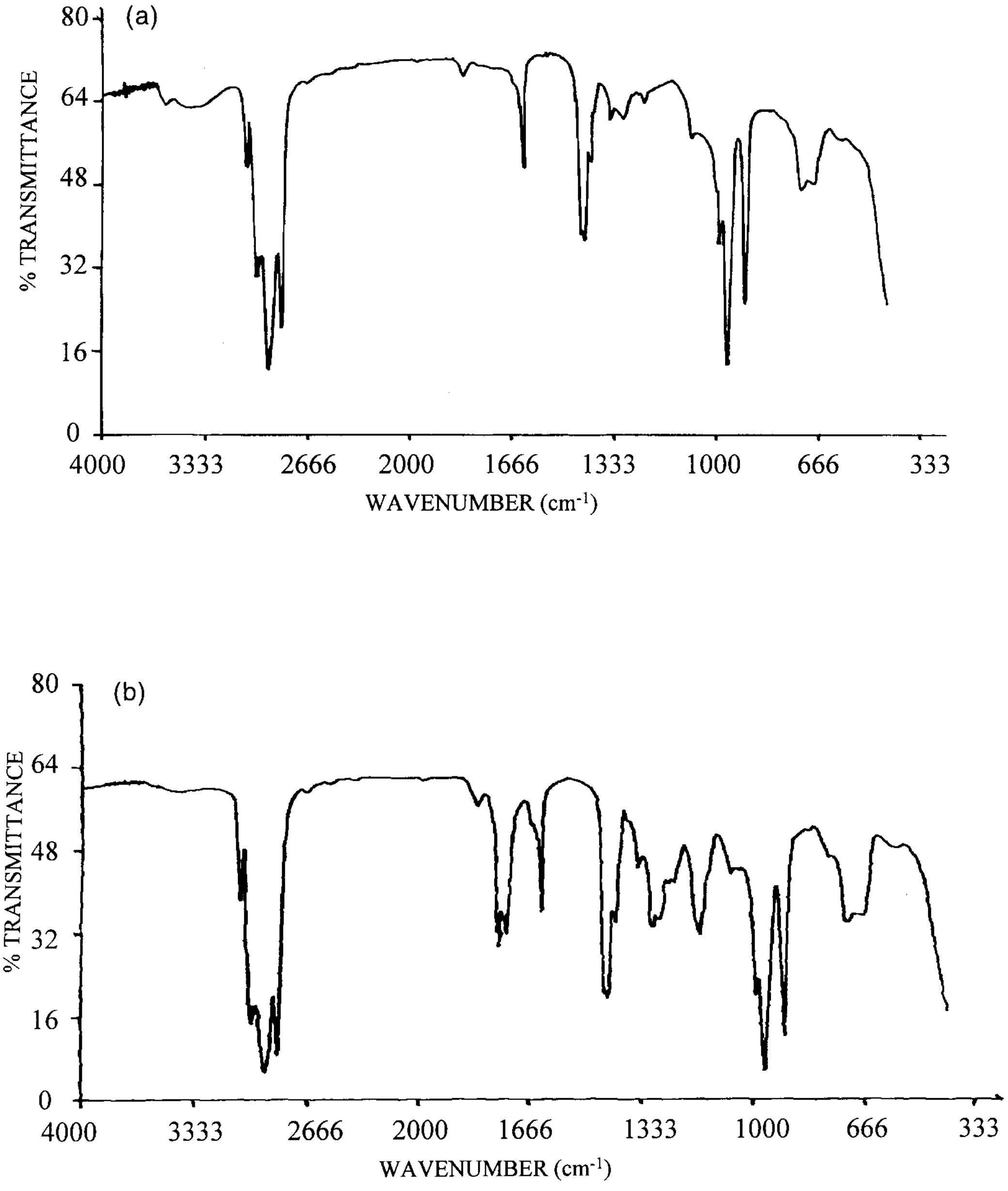

Fig. 1. The typical IR spectra of the hydroxyl-terminated oligomer HTPB before (a) and after (b) chloroacetyl reaction.

nature and radical mechanism and it has been used for the polymerization of a broad range of vinyl monomers and the synthesis of the polymers with well-controlled structure under mild conditions [4].

It is necessary for a well-controlled ATRP that the initiator (R—X) should be with an inductive or resonance group, such as benzyl, vinyl, carbon and some other groups on the α position of —X for the ATRP, and there is almost no limit on the structure of the alkyl (R—) [5], If a polymer with halogen acetyl end-group was used as a macro-initiator in the ATRP of vinyl monomers, it should be easy to get block copolymers with well-defined structure.

Based on this consideration, we have communicated a method to synthesize the ABA block copolymers containing polystyrene as A segment and some kind of polyether, polyester or polybutadiene as B segment [6]. In the former communication, a macro-initiator technique was employed. Some commercial hydroxyl-terminated oligomers, α,ω-hydroxyl-terminated polyether,

Table 1
Halogen analysis results of the oligomers with chloroacetyl end-group

P–Cl[a]	M_n	Functionality	$Cl_{th.}$(%)	$Cl_{exp.}$(%)
ET220–Cl	2000[b]	2	3.19	3.07
ES94718–Cl	2810[b]	2	2.38	2.39
HTPB–Cl	1913[c]	2.1–2.3	3.8–4.2	3.40

[a] ET220–Cl: α,ω-bichloroacetyl polyether based on ET220; ES94718–Cl: α,ω-bichloroacetyl polyester based on ES94718; HTPB–Cl: α,ω-bichloroacetyl polybutadiene based on HTPB.

[b] M_n based on hydroxyl number determination.

[c] GPC result calibrataed by PSt standards.

polyester and polybutadiene, were used to prepare α,ω–bichloroacetyl oligomers (P–Cl), and then the biochloroacetyl oligomers were used as the macroinitiators and copolymerized with styrene (St) to form ABA copolymers with polystyrene as A segment. After we first reported the synthetic method, a similar method to synthesize polysulfone-based and polyester-based ABA block copolymers was reported by Matyjaszewski's group [7–9]. Subsequently, Jankova et al. successfully synthesized PS-b-PEG-b-PS block copolymer by means of almost the same procedure [10].

In this paper, we will report the detailed synthesis of some ABA block copolymer such as PSt-b-polyether-b-PSt, PSt-b-polyester-b-PSt, and PSt-b-polybutadiene-b-PSt using hydroxyl-terminated oligomeric precursors through ATRP.

2. Experiment section

2.1. Materials

Ethylene oxide-capped poly(propylene oxide) polyether diol (PPO, ZS2185®, ethylene oxide content = 15%, $M_n = 2000$ g mol^{-1}; ET-2185) was obtained from Jingling Petrochemical Company. Poly(propylene oxide) polyether diol (PPO GE220®, $M_n = 2000$ g mol^{-1}; ET-220) was obtained from the No. 3 Chemical Factory of Gaoqiao, Shanghai. Dimethyl phthalate-based polyester diol ($M_n = 2810$ g mol^{-1}, hydroxyl number = 39.23, acid number = 0.63; ES-94718 was synthesized in our laboratory. Hydroxl-terminated polybutadiene (HTPB; $M_n = 6539$ g mol^{-1}, functionality = 2.1–2.3) was obtained from the Institute of Liming Chemical Industry. Chloroacetyl chloride was prepared according to the literature [11]. Copper chloride (CuCl) was obtained from the Chemical Regent Factory of Shanghai, and purified according to the literature [12]. 2, 2′-Bipyridyl (bpy) was commercially available and recrystallized several times from acetone and dried in vacuum before use. Styrene (St) was vacuum distilled over CaH_2 under argon atmosphere before polymerization.

2.2. The synthesis of α,ω–bichloroacetyl oligomer

The hydroxyl-terminated oligomer was reacted with chloroacetyl chloride in toluene under nitrogen atmosphere. The reaction was carried out without catalyst at 80°C for 10–20 h or at ambient temperature for 1 h using *N,N*-dimethyl benzylamine as catalyst. The catalyst was washed using diluted HCl solution.

2.3. The synthesis of ABA block copolymer

The general procedure was as follows: α,ω–bichloroacetyl oligomer, CuX and bpy were added in baked glass tube and sealed with a rubber septum. The glass tube was then degassed under vacuum and filled with argon. This was done three times. The degassed St was then added by syringe technique, then the mixture was immersed in an oil bath and heated at 130°C. After a certain time, the tube was opened and THF was added to the sample to dissolve the polymer.

2.4. Characterization

The conversion was determined gravimetrically. Molecular weights and molecular weight distributions were measured using Waters 150C-ALC/GPC with Waters Styragel® HT2, Styragel® HT4 columns. The molecular weight was calibrated by polystyrene standards. IR spectra were recorded using a Magna-IR spectrometer. H^1-NMR spectra were recorded using a JEOL FX-90Q instrument. Chlorine content was analyzed using a halogen analysis (Wireless Factory of Taixian, China); the sample was first decomposed using the oxygen bomb method.

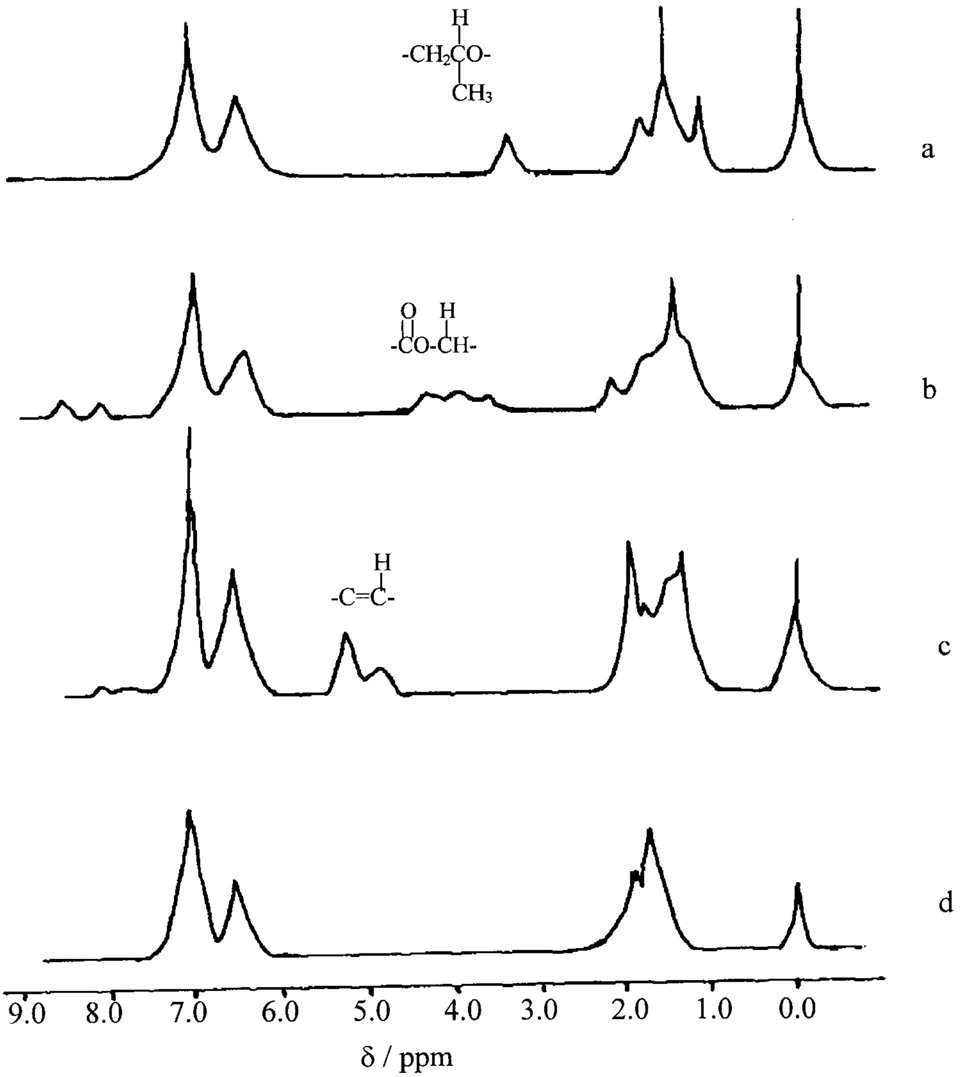

Fig. 2. H^1-NMR spectra of the ABA block copolymers and pure PSt (a: PSt-b-ET220-PSt; b: PSt-b-ES94718-PSt; c: PSt-b-HTPB-PSt; d: pure PSt).

3. Results and discussion

3.1. The synthesis of α,ω-bichloroacetyl oligomers

α,ω-bichloroacetyl oligomers were prepared through the acetyl reaction between the hydroxyl-terminated oligomers and chloroacetyl chloride. The oligomers before and after acetyl reaction were analyzed using IR spectroscopy. The typical IR spectra are shown in Fig. 1.

In Fig. 1a, the —OH absorption peak in the oligomer can be observed at 3300–3600 cm^{-1}. After acetyl reaction, the —OH peak disappeared and the absorption peak of C═O at 1760 cm^{-1} was observed correspondingly in the spectrum (Fig. 1b). The disappearance of the —OH peak in the IR spectra suggests that the —OH end-group of the oligomers has been converted completely into the chloroacetyl end-group.

Furthermore, the chlorine content of the α,ω-bichloroacetyl oligomers (P–Cl) was determined through the oxygen-bomb method; the results are illustrated in Table 1. As Table 1 shows, the experiment results of chlorine content in the α,ω-bichloroacetyl oligomers were in agreement with the theoretical values. The results further proved that the —OH end-group had been completely transferred to chloroacetyl end-

Table 2
GPC results on the macro-initiators and the block copolymers[a]

Precursor	Macro-initiator		Block copolymer		
	$M_n \times 10^{-4}$[e]	M_w/M_n	$M_{n.th} \times 10^{-4}$	$M_{n.GPC} \times 10^{-4}$	M_w/M_n
ET2185[b]	0.370	1.08	1.19	1.28	1.34
ET220[b]	0.283	1.28	1.19	1.26	1.58
ES94718[c]	0.626	1.55	1.21	1.23	1.48
HTPB[d]	0.654	1.97	2.04	1.90	2.16

[a] Reaction temperature: 30°C, P–Cl:CuCl:bpy = 1:1:3.
[b] polyether.
[c] polyester.
[d] polybutadiene.
[e] PSt as standard sample.

group, and that α,ω-bichloroacetyl oligomers (oligomer–Cl) had been produced.

3.2. The synthesis of ABA block copolymers

In order to synthesize ABA block copolymers, bulk polymerization of styrene was carried out using P–Cl (in Table 1) as macro-initiator in the presence of CuCl/bpy at 130°C. The resulted copolymers were refined and then analyzed using H^1-NMR spectrometry (Fig. 2). The NMR spectra of the block copolymers (Fig. 2) shows the identical shift at 6.2–7.3 ppm, which is assigned to the chemical shift of the pure polystyrene block. The characteristic peaks of polyether block, polyester block and polybutdiene block are at 3.6, 4.2 and 5.1 ppm, respectively. The NMR results indicate that these block copolymers contain both the polystyrene and oligomer segments.

The molecular weight and molecular weight distribution of the macro-initiators (P–X) and ABA block copolymers were analyzed using a GPC. All GPC traces showed a unimodal distribution. As Table 2 shows, the molecular weights of the block copolymers matched the theoretical values well. The theoretical values were calculated from the equation as follows:

$$M_{n,th} = (\Delta[M]/[\text{P–Cl}])M_W + M_0$$

where $\Delta[M]$,[P–Cl], M_w, and M_0 represent the con-

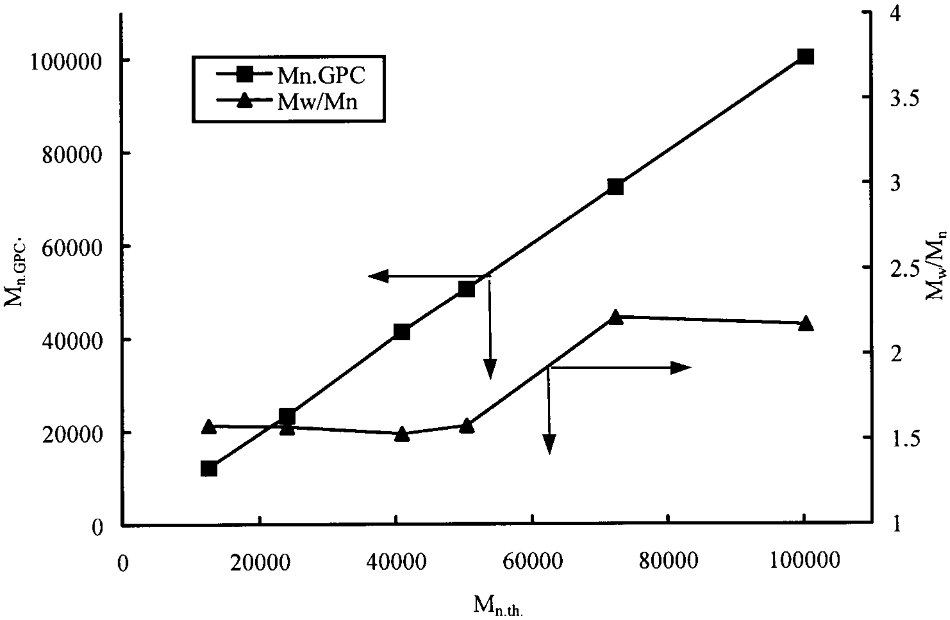

Fig. 3. Comparison of $M_{n.GPC}$ with $M_{n.th}$ for the bulk polymerization of styrene initiated by ET220–Cl:CuCl:bpy = 1:1:3 at 130°C.

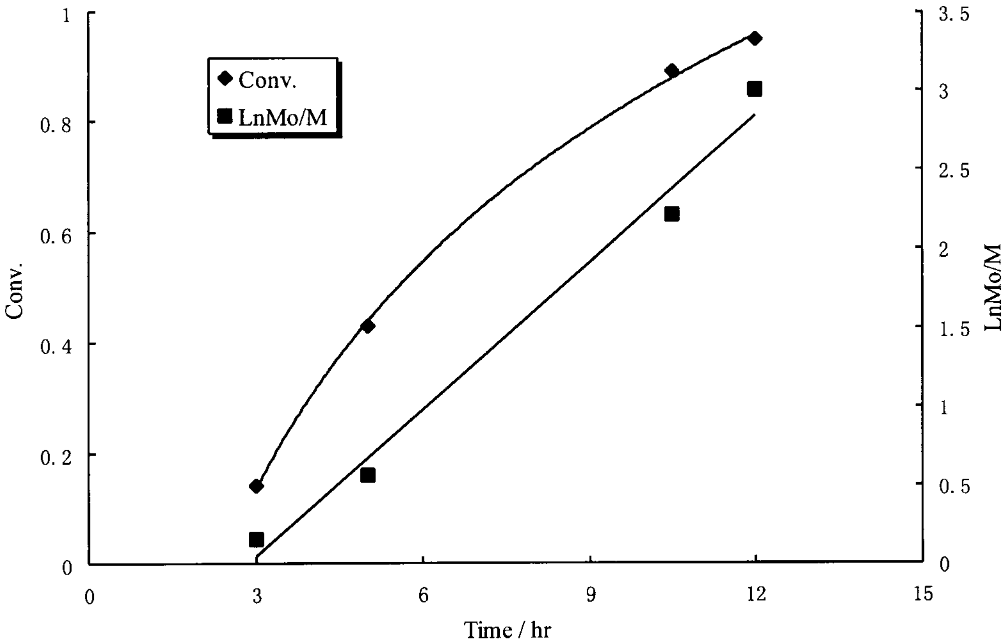

Fig. 4. The kinetics of the polymerization of St initiated by ET220–Cl (1 g) in the presence of CuCl/bpy (ET220–Cl:CuCl:bpy = 1:1:3) at 130°C.

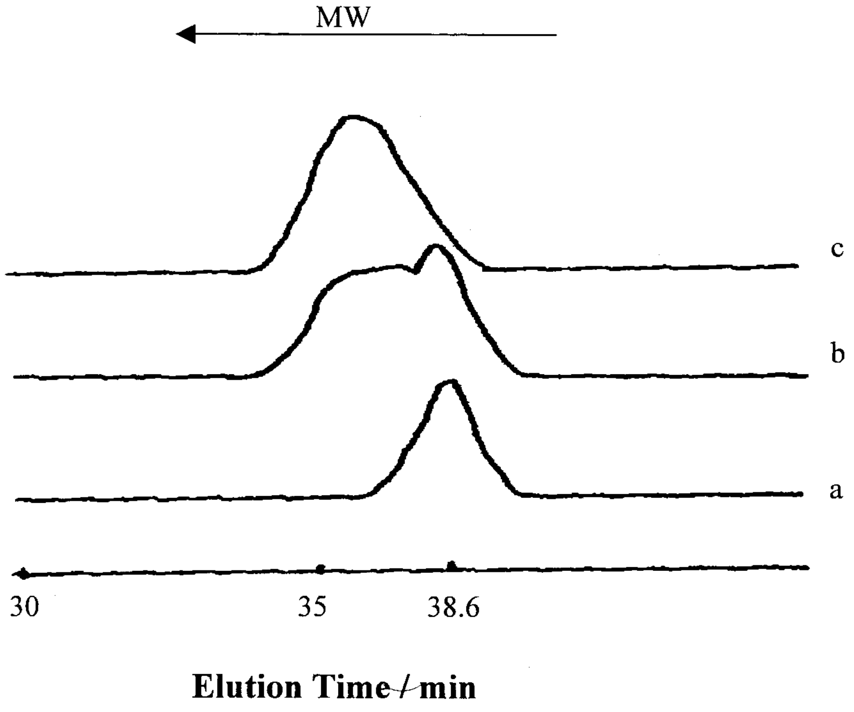

Fig. 5. The GPC traces of the macro-initiator (a) and the mixture after the polymerization had proceeded for 1 h (b) and 3 h (c), respectively.

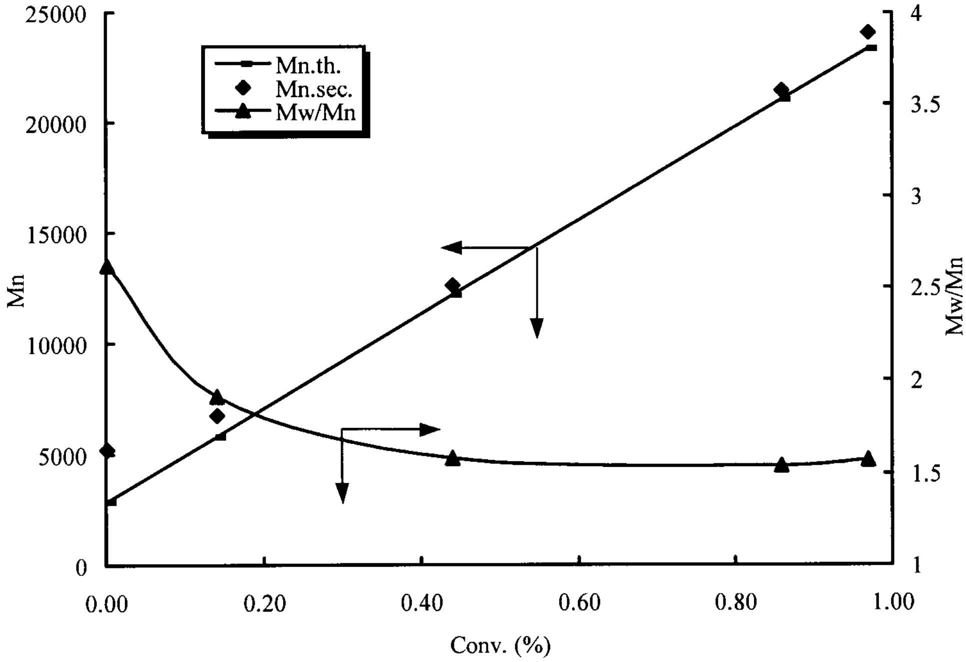

Fig. 6. Evolution of molecular weight, M_n, and molecular weight distribution, M_w/M_n, with monomer conversion for the bulk ATRP of styrene initiated by ET220–Cl:CuCl:bpy = 1:1:3 at 130°C.

sumed monomer, macro-initiator concentration, molecular weight of monomer, and molecular weight of macro-initiator, respectively.

Moreover, the molecular weight distribution of the ABA block copolymers was close to that of P–Cl. It implies that the polymerization proceeded in a 'living'/controlled nature.

Fig. 3 illustrates the correlation between the experimental molecular weight and the theoretical one as a linear plot up to 10^5. This provides evidence that the α,ω-bichloroacetyl oligomers (P–X) could act as efficient initiators and and that the number of the active chains remained constant during the polymerization. Broader molecular weight distributions were observed at higher molecular weights in Fig. 3. This might be caused by termination or slow deactive reaction of active species [12].

As the results of end-group transformation (Fig. 1, Table 1) and the polymerization (Table 2, Figs. 2 and 3), the methodology combining the transformation of hydroxyl end-group oligomers with hydroxyl end-group and the ATRP of St could be used to design the structure of the ABA block copolymers.

In order to further demonstrate the 'living' nature of the polymerization, the kinetics and the molecular weight control were studied for the polymerization of styrene with ET220-Cl)/CuCl/bpy.

As Fig. 4 shows, the linear relationship between the logarithm of monomer concentration and the reaction time suggests that the concentration of the active species was constant during the polymerization. A significant induction period can be observed in the case of polymerization of styrene initiated by ET220-Cl (Fig. 5) It is different to the ATRP of styrene initiated by low molecular weight initiators such as 1-phenylethyl chloride and ethyl-2-bromopropionate. The results implied that the slow initiation might be caused by the high molecular weight of the macro-initiator.

Aliquot mixtures of the polymerization system (ET220-Cl/CuCl/bpy) were analyzed using GPC after polymerization for 1 and 3 h. The GPC traces of the mixtures and the macro-initiator (ET220-Cl) are illustrated in Fig. 5. Fig. 5 shows that, after polymerization for 1 h, the GPC trace is similar to that of the macro-initiator, except that there is an increment in the content of high molecular weight, which suggests the existence of slow initiation. After the polymerization had proceeded for 3 h, the GPC trace became a normal distribution, and the molecular weight distribution (MWD) decreased simultaneously, suggesting initiation was complete.

Fig. 6 shows that the molecular weight of the product gradually increased gradually with the raising of monomer conversion, and matched the theoretical value. Simultaneously, the MWD narrowed with the extension of the polymerization. Both results of the kinetics and the molecular weight control indicated that the polymerization proceeded in a 'living'/controlled nature, although initiation is relatively slow.

4. Conclusion

A new method is proposed to synthesize some kinds of ABA block copolymers with well-defined structure by means of 'living'/controlled radical polymerization with α,ω-bichloroacetyl oligomers as macro-initiators. The macro-initiators were prepared by the transformation of hydroxyl end-group on some commercial oligomers into α,ω-bichloroacetyl end-group. Therefore, the ABA block copolymers can combine polystyrene segments with some different kinds of segments, such as polyether, polyester and polybutadiene. This method can be extended easily to form some new multi-armed or star-like copolymers based on multifunctional oligomers and vinyl monomers apart from styrene.

Acknowledgements

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