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RESEARCH ARTICLE

Synthesis and characterization of a novel well-defined comb-like ionomer

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A novel well-defined comb-like ionomer with cations was synthesized by the combination of living anionic polymerization and atom transfer radical polymerization (ATRP). The synthetic approach involves the coupling reaction of polystyrene (PS) backbone bearing 1,1-diphenylethene (DPE) pendant groups with living polystyryllithium (PSLi), subsequent amine functionalization of the resulting 1,1-diphenylmethyl anions with 3-dimethylaminopropyl chloride (DMAPC), and quaternization of tertiary amino groups with hydrochloric acid. The comb-like ionomer was characterized by ^{1}H NMR, IR, GPC measurements and end-group titrition.

Keywords coupling reaction, living anionic polymerization, comb-like ionomer, amine functionalization, quaternization

1 Introduction

Ionomers are a class of ion-containing polymers having ionic groups (mainly carboxylate, sulfonate, and quaternary ammonium salt) up to 10–15 mol% randomly distributed along nonionic backbone chains [1–3]. In the past 2 decades, ionomers have attracted increasing attention, thanks to the dramatic modification induced in the properties of polymeric materials by strongly interacting ions [4–14]. At present, the topical subjects studied on ionomer are preparation, self-assembly, and structure-property relationship.

Many types of ionomers such as random, ABA block, AB block and telechelic ionomers have been synthesized. The poorly controlled molecular structure and ionic distribution of ionomers does not favor an unambiguous characterization of their supermolecular structure and general behavior. Therefore, a search for model ionomers (the molecular structure and ionic distribution of which can be largely controlled) appear to be a very attractive goal. The telechelic ionomers containing two ion groups on two ends and block ionomers, as common model ionomers, have been extensively studied [15–21].

To spread the structure of model ionomers, herein, we describe a synthetic methodology to prepare a well-defined comb-like ionomer by ATRP and anionic polymerization. Scheme 1 illustrates our strategy for the preparation of the comb-like ionomer. The synthetic approach involves the coupling reaction of polystyrene (PS) backbone bearing 1,1-diphenylethene (DPE) pendant groups (**1**) prepared by ATRP with living polystyryllithium (PSLi), subsequent amine functionalization of the resulting 1,1-diphenylmethyl anions (**2**) with 3-dimethylaminopropyl chloride (DMAPC) to yield dimethylamino-functionalized polymer (**3**), and quaternization of **3** with hydrochloric acid to yield well-defined comb-like ionomer with cations (**4**).

2 Experimental

2.1 Materials

Styrene was purified by distillation over calcium hydride. Tetrahydrofuran (THF) was refluxed with a Na-K alloy and benzophenone until a characteristic blue color was evident, and distilled under a nitrogen atmosphere. 1,3-bis(dimethylamino)propyl chloride (DMAPC) was dried with calcium hydride for at least 3 days and distilled just before use. Other reagents were not purified before use.

2.2 Measurements

^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer with $CDCl_3$ as a solvent and tetramethylsilane as the internal reference. IR spectra were recorded on a 20SX spectrometer with KBr pellets. GPC measurements were carried out in THF (1 $mL \cdot min^{-1}$) at 35°C using a Waters 515 liquid spectroscopy equipped with three styragel columns and a refractive index and SL detector. Monodisperse PS samples were used as standards for calibration. The refractive index increments (dn/dc) of the graft copolymers were determined in THF with a laser source operating at 633 nm at 25°C. The concentrations of the amine chain end-groups in the amine-functionalized polymers were determined by titration in a 1/1 (v/v) mixture of chloroform and glacial acetic acid with perchloric acid as the titrant and methyl violet as the indicator.

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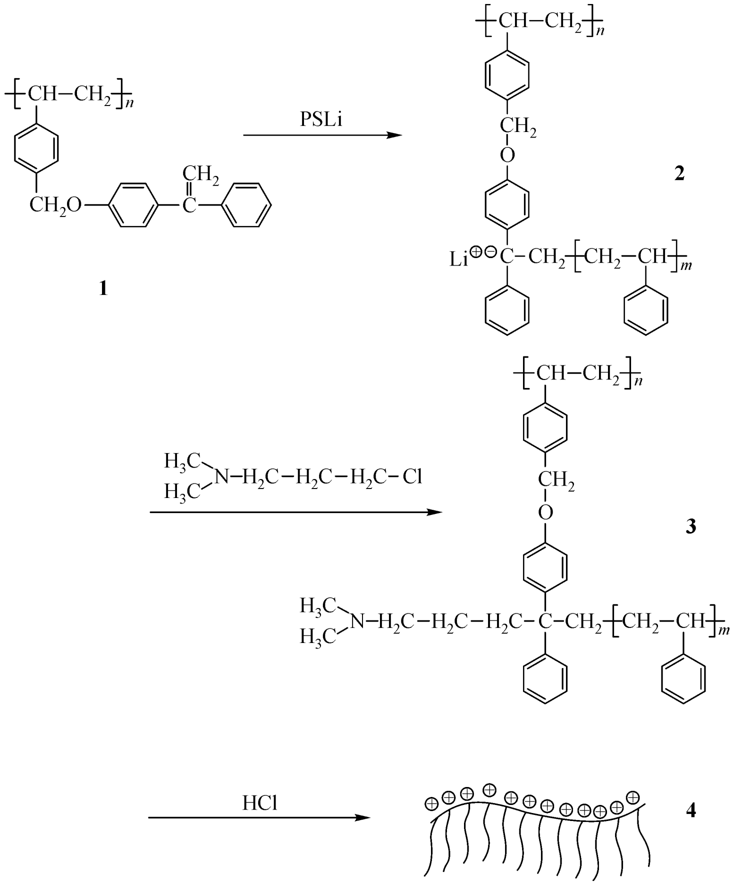

Scheme 1 Synthetic route of the comb-like ionomer.

2.3 Synthesis of **1**

The backbone PS bearing 1,1-diphenylethylene (DPE) pendant groups (**1**) was synthesized according to the method described by Li et al. [22].

2.4 Synthesis of **3**

The anionic polymerization of styrene was performed at −78°C with *n*-butyllithium (*n*-BuLi) as an initiator and THF as a solvent. In half an hour, an aliquot of polymer solution was taken out for GPC measurement. Subsequently, the resulting living polystyryllithium PSLi was introduced quickly into a solution of **1**. The reaction was carried out for 1 h to yield **2**, and an aliquot of polymer solution was taken out for measurement. Then an excess of DMAPC was added and the reaction was carried out at room temperature for 3 h. The polymer **3** was isolated by precipitation into methanol and dried in vacuo for 12 h.

2.5 Synthesis of **4**

Quaternization of **3** with hydrochloric acid was carried out in THF. The polymer **3** concentration was 5 *w*/*v* %, and the molar ratio of 1 $\text{moL}\cdot\text{L}^{-1}$ hydrochloric acid to the tertiary amino group of **3** was 5∶1. After reaction, the quaternized polymer **4** was precipitated with methanol and dried for 12 h.

3 Result and discussion

3.1 Coupling reaction

The coupling reaction of PSLi and **1** was carried out at −78°C by adding quickly the PSLi solution into a known amount of **1**, previously vacuum dried and dissolved in dry THF. To achieve a high coupling yield, a slight excess of PSLi toward DPE function of **3** ($[\text{PSLi}]_0$ / $[\text{DPE}]_0$ = 1.2) was used. A rapid color change from orange to deep red was observed, suggesting that the formation of diphenylmethyl anions occurred rapidly.

Figure 1(b) shows the GPC spectroscopy of crude graft polymer precursor (PS-g-PS) obtained from **2** by quenching with methanol. The peak ascribed to PS-g-PS is sharp monodal and very narrow (M_w/M_n = 1.20), suggesting a homogeneous and clean grafting. The peak at low molecular weight is ascribed to the PS branch since its M_n and M_w/M_n

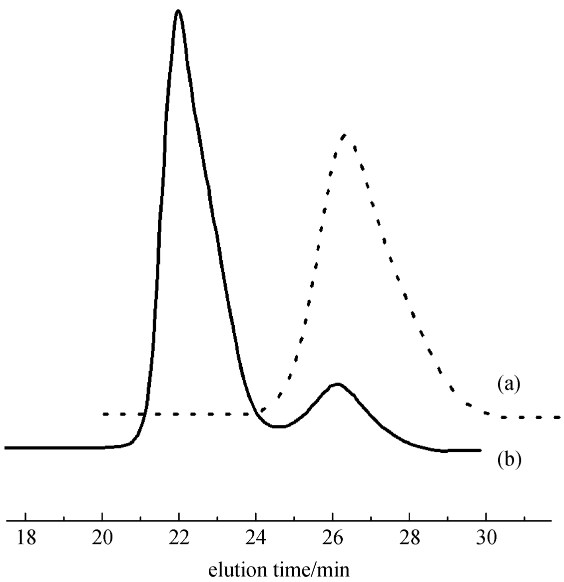

Figure 1 GPC spectroscopy of PS-g-PS obtained from **2** by quenching with methanol (a) PS precursor and (b) graft polymer precursor PS-g-PS.

are identical to those of the initial living PSLi (Figure 1(a)). This formation is likely due to the PSLi excess and some deactivation of PSLi carbanions by the impurities remaining in the **1** solution.

Figure 2(a) shows the ^{1}H NMR spectrum of the above-mentioned fractionated PS-g-PS. Compared with the ^{1}H NMR spectrum of **1** (see Figure 2(b)), the resonance at 5.29 ppm corresponding to vinyl protons disappeared completely. Instead, a new signal was observed at 3.52 ppm for the terminal methine proton in the coupling product; integration of the area of this signal relative to the area of the resonances at 4.91 ppm corresponding to the methylene protons adjacent to the ether linkage gave a value of 1:2.1 (theoretical value 1:2), suggesting the nearly full addition of DPE groups by the PSLi.

3.2 Amine functionalization

After coupling reaction of **1** and PSLi, the excess DMAPC was added to solution at −78°C by syringe. The deep red maintained in 2 h. Also, once the reactor was shifted to room temperature, the deep red became light quickly, and finally colorless by light yellow, suggesting that the reaction of diphenylmethyl anions of **2** and DMAPC was slow at −78°C, while quick at room temperature.

Figure 3 shows the GPC spectroscopy of polymers before (a) and after (b) amine functionalization. The GPC profiles (a) and (b) were very similar in shape and retention time, and no dimer formation was observed, suggesting the side reaction did not occur during the reaction. The purified **3** was obtained by fractional precipitation using tolune/methanol (see Figure 3(c)).

The ^{1}H NMR spectrum of purified dimethylamino-functionalized comb-like polymer **3** exhibited a peak at 2.37 ppm (see Figure 4), which is not observed for the graft polymer precursor (PS-g-PS) obtained from **2** by quenching with methanol (see Figure 2(a)). This peak was assigned to the methyl protons in the $-\mathrm{N(CH_3)_2}$ group by analogy with the dimethylamino-functionalized linear polystyrene [23].

The concentrations of amine of **3** were analyzed by titration using perchloric acid as the titrant and methyl violet as the indicator. A rapid color change from purple to brilliant blue was observed, suggesting that a terminal point came. The yield of amine functionalization could be calculated by the following formula:

$$FY = \frac{(V - V_0) \times N_{\mathrm{HClO_4}}}{\frac{m}{\overline{M_\mathrm{n}}} \times \overline{DP}} \times 100\%$$

where FY was the yield of amine functionalization, and V and V_0 were the volumes of perchloric acid consumed by samples and void test, respectively. $N_{\mathrm{HClO_4}}$ was the concentration of perchloric acid, m was mass of sample, and $\overline{M_n}$ and $\overline{DP}$ were the number average molecular weight of sample and degree of polymerization of polymer **1** respectively. The results suggested that the yield of amine functionalization were almost quantitative (see Table 1).

The characteristics of dimethylamino-functionalized comb-like polymer **3** are given in Table 1. Because of its branched architecture, the apparent molecular weight of **3** determined by GPC equipped with RI detector is not reliable. The absolute molecular weight of **3** was therefore determined by GPC equipped with SL detector after measuring the specific dn/dc value of **3**. This value is very close to the corresponding theoretical one calculated assuming that all the DPE groups of **1** were coupled with living PSLi. This supports that the grafting is nearly complete.

3.3 Quaternization

The comb-like ionomer with cations **4** could be synthesized by quaternization of tertiary amino groups of **3** with hydrochloric acid or alkylhalogens. The yield of quaternization also could be determined by titration using perchloric acid as the titrant and methyl violet as the indicator. The volumes of perchloric acid consumed by samples and void test were almost the same, suggesting that the yield of quaternization was nearly quantitative.

Figure 5 shows the GPC spectroscopy of polymer **3** (a) and

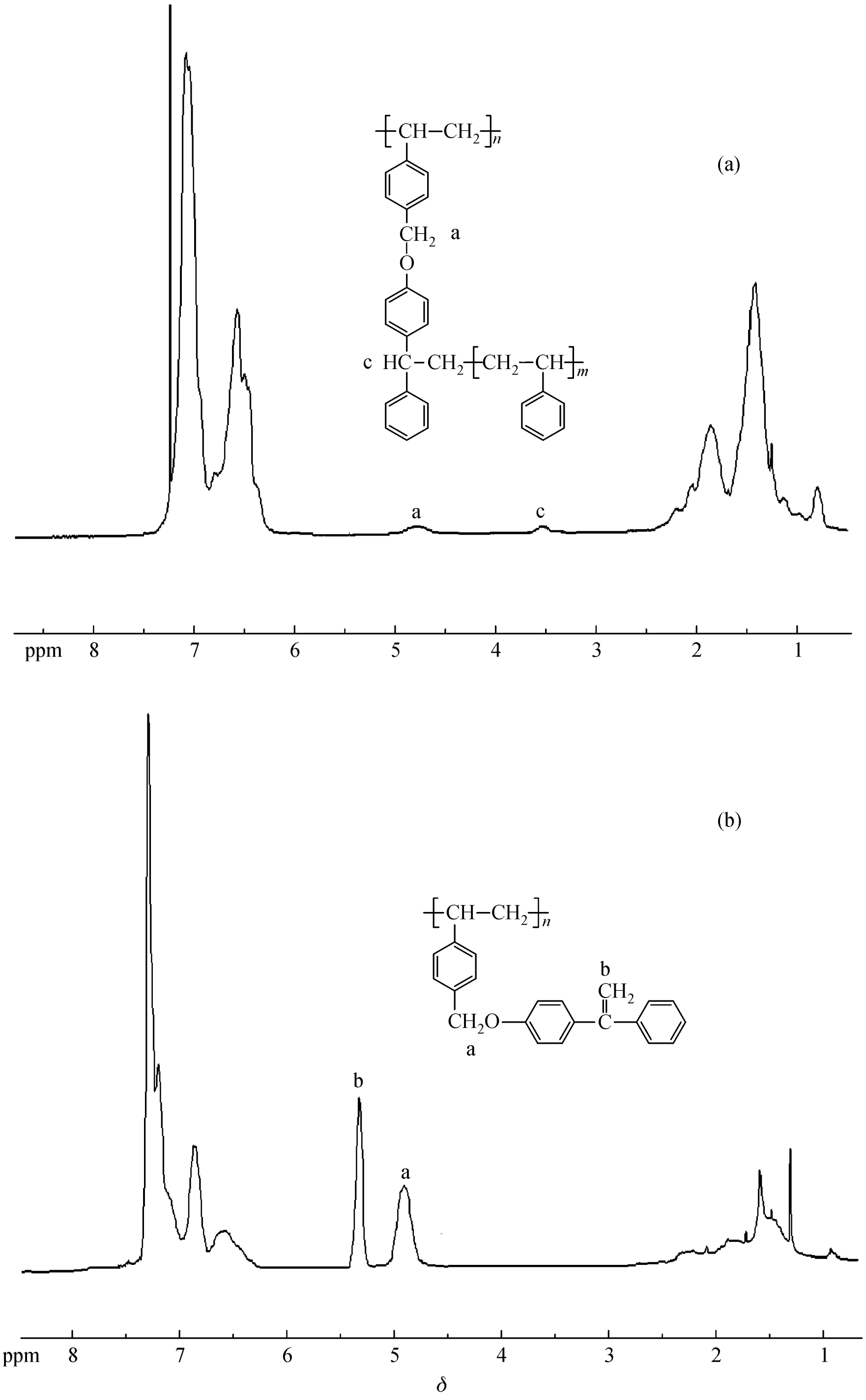

Figure 2 (a) ^{1}H NMR spectroscopy of fractionated PS-g-PS obtained from **2** by quenching with methanol. (b) ^{1}H NMR spectroscopy of **1**.

4 (b). As we can see, the retained time of the GPC profile of polymer after quaternization lagged clearly, and the shape of the profile was wider, which were likely because of the special ions interaction.

4 Conclusions

In conclusion, a well-defined comb-like ionomer with cations was synthesized successfully by three steps involving the

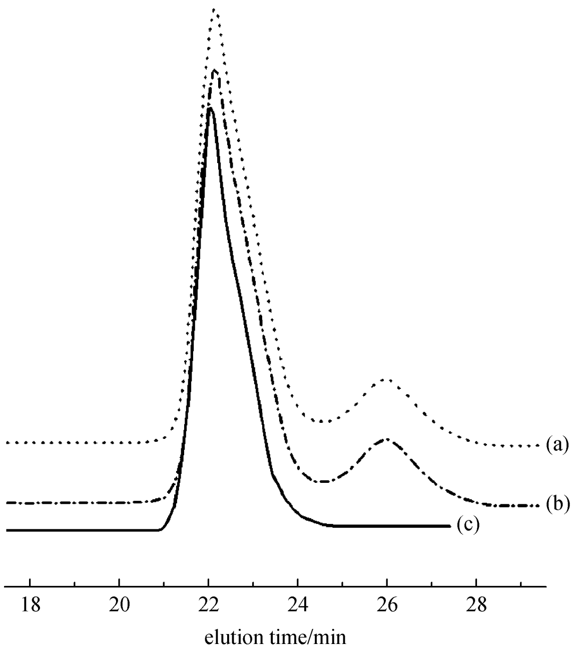

Figure 3 GPC spectroscopy of **3** (a) PS-g-PS obtained from **2** by quenching with methanol (b) crud product of **3** (c) fractionated **3**.

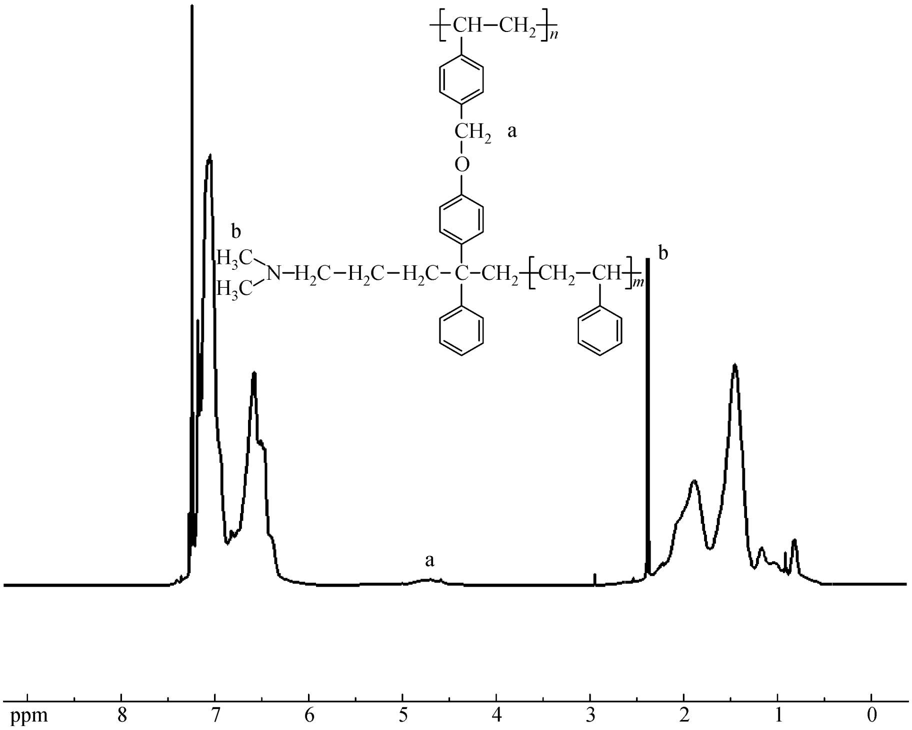

Figure 4 The ^{1}H NMR spectroscopy of dimethylamino-functionalized comb-like polymer **3**.

Table 1 Characterization of the dimethylamino-functionalized comb-like polymer **3**a)

Sample	living PS			amino-functionalized comb-like polymer			
	M_na)			$M_\mathrm{n} \times 10^{-3}$	$M_\mathrm{w}/M_\mathrm{n}$e)	*GE*f)/%	*FY*/%
	Theo.b)	LS detectorc)	RI detectord)				
1	2890	57.65	57.33	42.0	1.14	99.4	98.5
2	5600	106.33	107.9	54.3	1.12	100	99.0

a) Molecular weight of PSe: $M_\mathrm{n} = 5630$, $M_\mathrm{w} = 6750$, DP = 18, $M_\mathrm{w}/M_\mathrm{n} = 1.20$
b) Calculated assuming all DPE groups of backbone were coupled with PSLis
c) Examined by GPC with LS detector
d) Examined by GPC with RI detector
e) Examined by GPC
f) Graft efficiency, based on the molecular weight determined by GPC with LS detector
g) Functionalized yield determined by titration

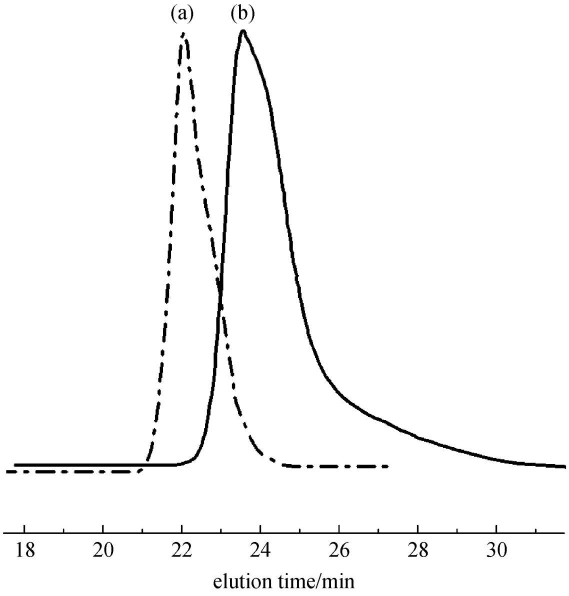

Figure 5 GPC spectroscopy of (a) **3** and (b) **4**.

coupling reaction of PS backbone bearing DPE pendant groups with PSLi, subsequent amine functionalization of the resulting 1,1-diphenylmethyl anions with DMAPC, and quaternization of tertiary amino groups with hydrochloric acid. The resulting end-group titration suggested that the yields of amine functionalization and quaternization were almost quantitative.

The resulting ionomers can form micelles by self-assembly, and the study of morphologies and solution behavior of the ionomer will be reported in the future.

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