

Preparation of PMMA–PS–PMMA via Combination of Anionic and Photoinduced Charge-Transfer Polymerization

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Received 12 November 1998; accepted 22 March 1999

ABSTRACT: PMMA–PS–PMMA triblock copolymers were prepared by the combination of an anionic mechanism with charge-transfer polymerization. Polystyrene with aromatic tertiary amino groups at both ends (PS_{ba}) was synthesized first by the reaction of a living polystyrene macrodianion with excess *p*-(dimethylamino)benzaldehyde; then, the PS_{ba} was constituted into a binary system with benzophenone (BP) to initiate the polymerization of methyl methacrylate (MMA) under UV irradiation. The intermediate and resulting block copolymers were characterized by GPC, IR, and ¹H-NMR. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2072–2076, 1999

Key words: anionic; charge-transfer polymerization; ABA triblock copolymer; polystyrene; poly(methyl methacrylate)

INTRODUCTION

Recently, the preparation of block copolymers with complicated and controlled architectures has been a subject of interest, because some novel phenomena and properties can be observed from them.¹ Essentially, two kinds of methods can be used to synthesize block copolymers: One is living polymerization systems, including the well-known anionic polymerization, cationic polymerization,² group-transfer polymerization,³ and “living” controlled radical polymerization.^{4,5} The other is to combine different polymerization techniques together, such as anionic polymerization with cationic,⁶ anionic with Ziegler–Natta⁷ coordinate polymerization,

and anionic with radical⁸ polymerization. By means of the latter method, some special block copolymers which are impossible to prepare by a single polymerization method can be obtained.

Burgess et al. reported on the preparation of PS-*b*-PTHF via the combination of anionic with cationic polymerization.⁹ The living polystyrene (PS) macroanions were terminated by excess bromine first, then the latter were reacted with silver salt; the formed cations initiated the polymerization of THF.

Yagci et al.¹⁰ described the synthesis of a block copolymer of cyclohexene oxide and styrene (St) by a combination of radical and cationic polymerization. In this presentation, the preparation of PMMA–PS–PMMA, by a binary initiation system composed of PS with tertiary amine groups at both ends and BP under UV irradiation, is described, which has universal significance for the preparation of other special block copolymers^{11,12} that were impossible to make by the common anionic technique.

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Contract grant sponsors: Natural Science Foundation of China; Doctor Training Foundation of State Education Ministry of China.

Journal of Applied Polymer Science, Vol. 74, 2072–2076 (1999)

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CCC 0021-8995/99/082072-05

EXPERIMENTAL

Materials

St was dried with calcium hydride, then distilled under reduced pressure. Tetrahydrofuran (THF) was refluxed over solid KOH, then distilled from calcium hydride. Naphthalene (Shanghai Yuanhang Chemical Factory, Shanghai, China), *p*-(dimethylamino)benzaldehyde (DMAB; Shanghai Third Regent Factory, Shanghai, China), and benzophenone (BP) (Beijing Chemical Factory, Beijing, China) were recrystallized twice from ethanol. Methyl methacrylate (MMA), *N,N*-dimethylaniline (DMA), and benzene were purified by the usual way.

Anionic Polymerization of St Using Lithium Naphthalenide as Initiator

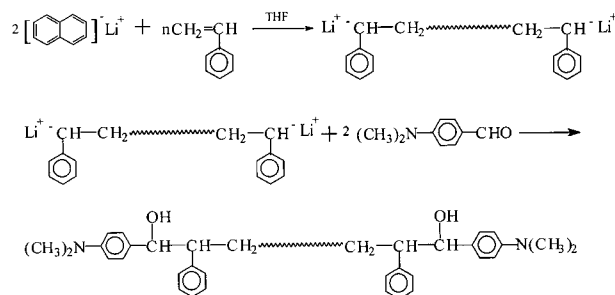
Lithium naphthalenide was synthesized by reacting naphthalene with lithium in anhydrous THF according to the procedure described in the literature.¹³ The concentration was 1.4 mol/L. Anionic polymerization of St was performed with lithium naphthalenide in THF at -78°C for 0.5 h.

Chain-end Functionalization Reaction of PS Macro dianion with DMAB

The above-mentioned living macrodianion solution of 60 mL (2.09×10^{-2} mol/L) was added dropwise to DMAB 0.895 g (6.01×10^{-3} mol) at -50°C in 20 min. The system was stirred for 0.5 h at room temperature and the reaction then stopped with excess methanol. The product (PS_{ba}) was purified by the procedure of repeated dissolving/precipitating with chloroform/methanol and dried at 60°C for 4 h.

Preparation of PS with Aromatic Tertiary Amine at One End (PS_{s})

PS with aromatic tertiary amine at one end (PS_{s}) was prepared by the reaction of DMAB with poly-



Scheme 1

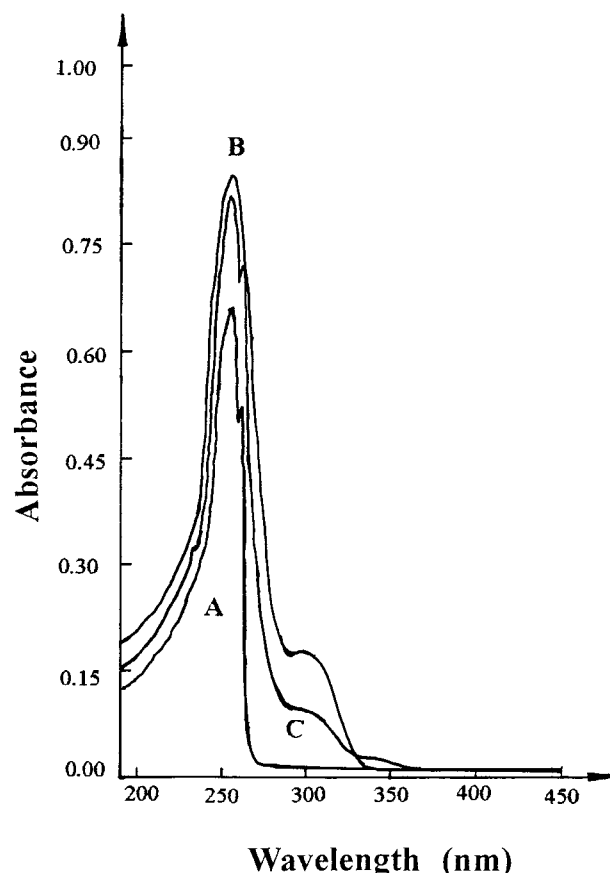


Figure 1 UV spectra of (A) PS, (B) DMA, and (C) PS_{ba} (solvent: CHCl_3 , [PS]: 1.7×10^{-5} mol/L; [DMA]: 6.3×10^{-5} mol/L; [PS_{ba}]: 1.2×10^{-5} mol/L).

(styryl)lithium obtained from *n*-butyllithium-initiated polymerization of St according to the method in the literature.¹⁴

Photoinduced Charge-transfer Polymerization of MMA

In a 100-mL ampule, PS_{ba} 0.288 g (4×10^{-5} mol), BP 0.0146 g (8×10^{-5} mol), MMA 5 mL, and benzene 5 mL were placed and the ampule was degassed three times by freeze-pump-thaw cycles and then sealed under N_2 . After that, it was irradiated by a high-pressure mercury lamp (DDZ-300, from Shanghai Yaming Lamp Factory) at 25°C for 9.5 h. A cupric sulfate aqueous solution was used as a photofilter to obtain the 365-nm monochromatic light. The desirable products were precipitated with methanol and purified by extracting for 24 h with cyclohexane to remove the unreacted PS_{ba} .

Table I Data of Block Copolymerization

Run	Initiator Type	Concentration of Initiator ($\times 10^{-3}$ mol L $^{-1}$)	Conversion of MMA ^e (%)	Conversion of PS ^b (%)	Block Copolymer	
					M_n^c ($\times 10^{-4}$)	M_w/M_n
1	DMA ^d	8	25.2	—	3.3	2.5
2	PS _s ^e	8	17.6	39.2	3.7	1.9
3	PS _{ba} ^f	4	27.6	34.6	15	2.8

[BP]: 8×10^{-3} mol L $^{-1}$; MMA: 5 mL; Benzene: 5 mL; polymer time: 9 h.

^a wt % = weight of reacted monomer (g)/weight of total added monomer (g).

^b Determined by GPC comparing the peak area of unreacted PS_b and the block copolymer.

^c Obtained by GPC based on the calibration with polystyrene standards.

^d DMA: *N,N*-dimethylaniline.

^e PS_s: polystyrene with aromatic tertiary amino group at one chain end, $M_n = 8000$.

^f PS_{ba}: polystyrene with aromatic tertiary amino groups at both chain ends, $M_n = 7200$.

Measurements

The molecular weight and molecular weight distribution of the polymer and copolymers were measured with a Shimadzu LC-3A gel permeation chromatograph equipped with a UV detector using CHCl₃ as an eluent and monodistribution PSs as standards. UV spectra were recorded on a 756 MC UV-vis spectrophotometer (Shanghai Third Analytical Instrument Factory). FTIR spectra were scanned by a Perkin-Elmer 983G spectrometer. ¹H-NMR spectra were scanned on a JEOL FX-90Q spectrometer using CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal standard.

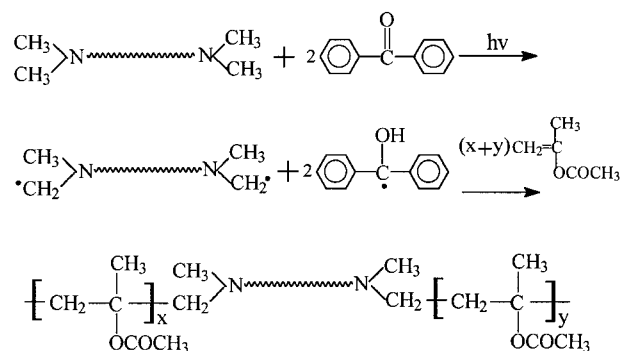
RESULTS AND DISCUSSION

Preparation and Characterization of α,ω -(dimethylamino)polystyrene (PS_{ba})

PS_{ba} was obtained by the capping of the living PS macrodianion with excessive DMAB, which is shown in Scheme 1. It was observed that the brown-red color of the living PS solution almost immediately turned to orange-yellow when it was dropped into the DMAB, and the reaction was carried out rapidly.

The UV spectrum of the capped PS is shown in Figure 1(C). In comparing the PS (A) and DMA (B), the typical absorption bands of $\pi \rightarrow \pi^*$ at 260 nm for the benzene ring and $n \rightarrow \pi^*$ at 315 nm for the aromatic tertiary amino groups in (C) appeared. To determine whether one end or both ends of the PS macrodianions were capped, the

linear relationship of the concentration of DMA versus its corresponding absorbance was plotted first and then the molecular weight of capped PS obtained by UV spectra ($M_n = 2 W_c / C_c$; here, M_n is molecular weight of PS_{ba}; W_c , the weight of PS_{ba}; and C_c , the concentration of PS_{ba} derived from UV spectra and the linear relationship of the concentration of DMA versus its corresponding absorbance) was compared with the value obtained by GPC. If the molecular weight of the former is twice as much as that of the latter, it means that only one end of the PS macrodianions was capped; if both of them were nearly the same, then both ends of the PS macrodianions were capped. The experimental results showed that the former was 7600 and the latter was 7200. Thus, it can be concluded that in our system both ends of the PS macrodianions were capped. The efficiency was about 95%.

**Scheme 2**

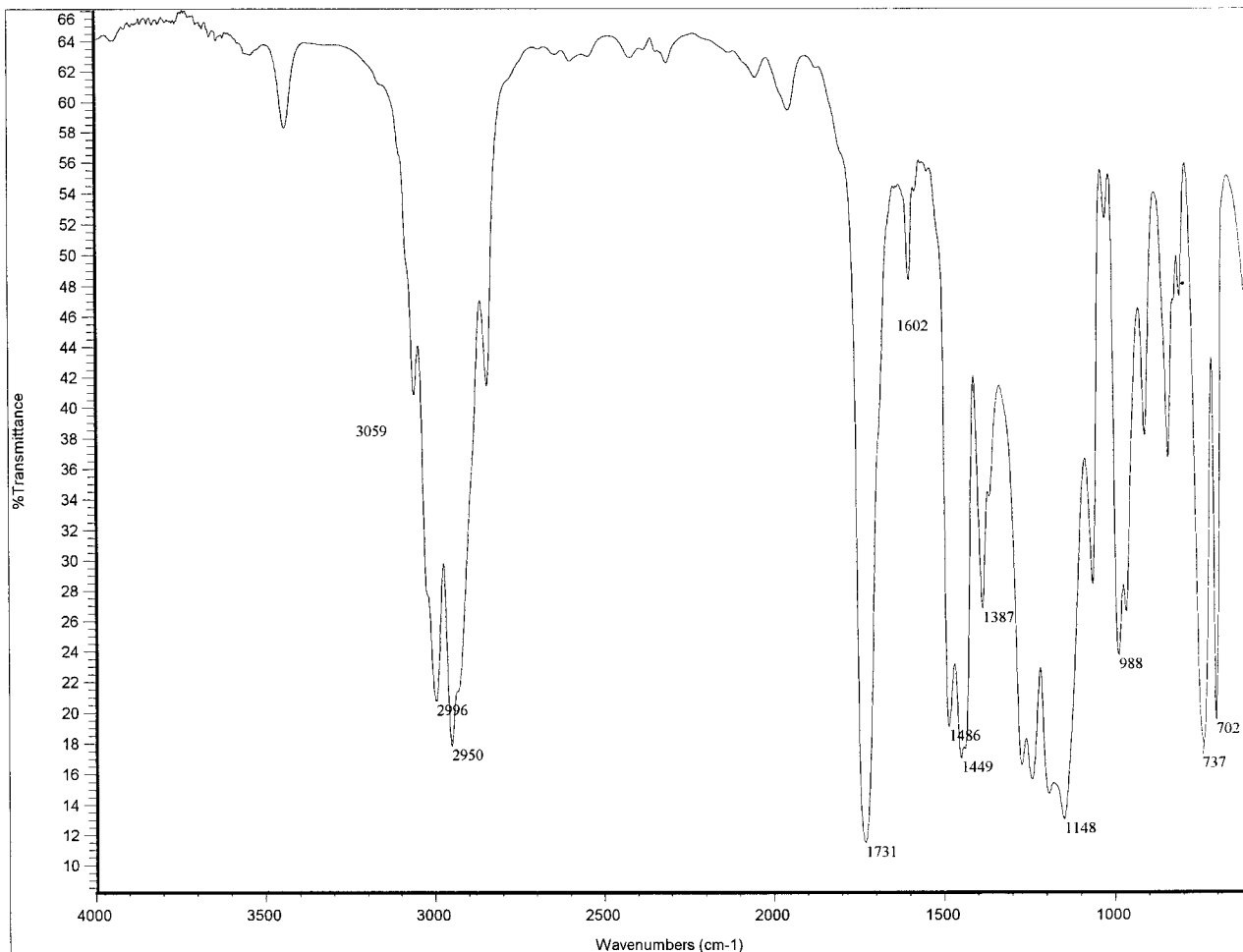


Figure 2 IR spectrum of PMMA-*b*-PS-*b*-PMMA.

Preparation and Characterization of PMMA-PS-PMMA

As a small binary initiation system composed of tertiary amine and BP,^{15,16} PS_{ba} also constituted complexes with BP under UV irradiation. Then, the diphenyl methanol radical and aromatic tertiary amine radicals of PS_{ba} were produced by a single-electron transfer and then by proton transfer. The former radical is stable in our system and serves as a chain terminant,¹⁷ and the latter initiated the polymerization of MMA according to the equations in Scheme 2.

The data on copolymerization using the different initiation systems are summarized in Table I. When small binary initiation systems such as DMA/BP and PS with the aromatic tertiary amine at one end (PS_s)/BP, were used, in the same conditions, the molecular weights of PMMA

for both of them were rather close each other (runs 1 and 2). When the PS_{ba}/BP was used, although the concentration of PS_{ba} was about one-half that of PS_s, the molecular weight of the PMMA segments is much higher than that of PMMA in runs 1 and 2. It revealed that, in the binary initiation system of PS_{ba}/BP, the species were bis-radicals and the propagation of MMA was conducted from both ends of the PS. Therefore, the resulting block copolymers were expected to be mainly of the ABA type.

The object copolymers were characterized by IR and NMR and the results are shown in Figures 2 and 3. The appearance of benzene ring peaks of the PS block at 3059, 1602, 1489, 1449, and 702 cm⁻¹ in IR and the chemical shift at 7.01–6.52 ppm in NMR and the carbonyl peak at 1731 cm⁻¹ in IR and CH₃O— at 3.60 ppm and CH₃— at

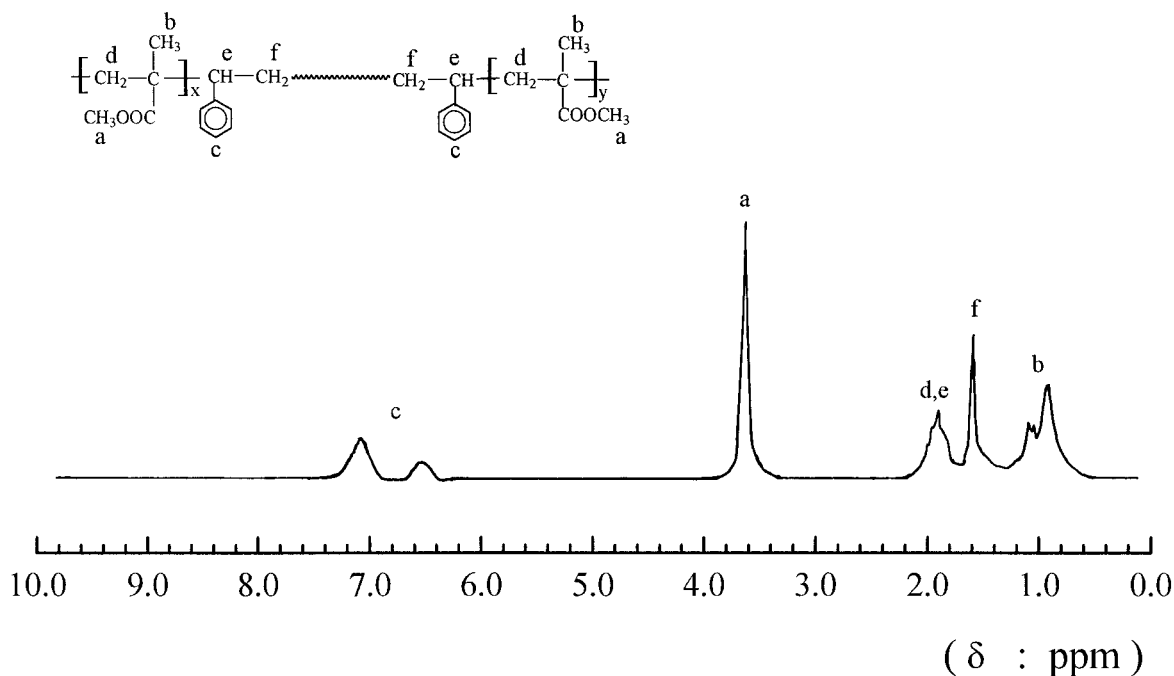


Figure 3 ¹H-NMR spectrum of PMMA-*b*-PS-*b*-PMMA.

1.05–0.76 ppm in NMR for the PMMA block confirmed the existence of PS and PMMA segments in the object copolymers.

The authors acknowledge the financial support from the Natural Science Foundation of China and the Doctor Training Foundation of State Education Ministry of China.

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