

Synthesis and Properties of Polystyrene-*b*-poly(ethylene oxide)-*b*-polystyrene Triblock Copolymers

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ABSTRACT: A series of well-defined and property-controlled polystyrene (PS)-*b*-poly(ethylene oxide) (PEO)-*b*-polystyrene (PS) triblock copolymers were synthesized by atom-transfer radical polymerization, using 2-bromo-propionate-end-group PEO 2000 as macroinitiators. The structure of triblock copolymers was confirmed by ¹H-NMR and GPC. The relationship between some properties and molecular weight of copolymers was studied. It was found that glass-transition temperature (T_g) of copolymers gradually rose and crystallinity of copolymers regularly dropped

when molecular weight of copolymers increased. The copolymers showed to be amphiphilic. Stable emulsions could form in water layer of copolymer–toluene–water system and the emulsifying abilities of copolymers slightly decreased when molecular weight of copolymers increased. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 727–730, 2006

Key words: PS-*b*-PEO-*b*-PS; atom-transfer radical polymerization (ATRP); glass-transition temperature (T_g); crystallinity; amphiphilic

INTRODUCTION

Block copolymers are of considerable interest for various applications, such as emulsifiers, dispersion stabilizers, compatibilizers, biological material, phase transfer catalyst, and water-absorbing elastomer.^{1–4} Traditionally, block copolymers are made by anionic, cationic, and group-transfer polymerization methods; however, these polymerization methods can be successfully carried out only under strictly controlled conditions.⁵ Pai-Panandiker et al.⁶ prepared PS-*b*-PEO copolymer by conventional free radical polymerization, but the molecular weight distribution of copolymers was wide. Recently, “living”/controlled radical polymerization reactions have been studied intensively as methods of preparing block copolymers,⁷ among which atom-transfer radical polymerization (ATRP) is considered as a successful and versatile way. Shiyuan Cheng⁸ and Jankova¹ groups obtained well-defined PS-*b*-PEO-*b*-PS triblock copolymers by ATRP. Some properties of copolymers containing PS and PEO chains were also reported,⁹ for example, star-shaped and dendrimer-like copolymers based on polystyrene core and poly(ethylene oxide) corona showed to be amphiphilic¹⁰; the end groups of PEO-

b-PS-*b*-PEO triblock copolymers in toluene were found to be adsorbed on the surface of a silicon wafer with an oxide layer, leaving the PS block dangling in the solution.¹¹ Aqueous PEO-*b*-PS-*b*-PEO or PEO-*b*-PS micelles were self-assembled spherical structures with a core of PS phase surrounded by a water-swollen corona of PEO chain, and could vary the block lengths by solvents.¹² However, properties of PS-*b*-PEO-*b*-PS copolymers are less reported.

In this work, low polydispersity PS-*b*-PEO-*b*-PS triblock copolymers were synthesized by ATRP. The glass-transition temperature (T_g), the crystallinity, the emulsifying abilities of triblock copolymers, and the relationship between these properties and the molecular weight of copolymers have been studied.

EXPERIMENTAL

Materials and analysis

2-Bromo-propionate-end-group PEO 2000 was prepared according to the method of Jankova et al.¹ CuBr, bipyridine, styrene, and tetrahydrofuran (THF) were supplied by the First Reagent Company of Shanghai (China). Styrene was stirred over CaH₂ overnight and vacuum-distilled before use. THF was purified by distillation before use. All other reagents were purchased from commercial sources and used without further purification.

Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded on an INOVA 400MHz (Varian Co., San Francisco, CA) using CDCl₃ as a solvent. Gel

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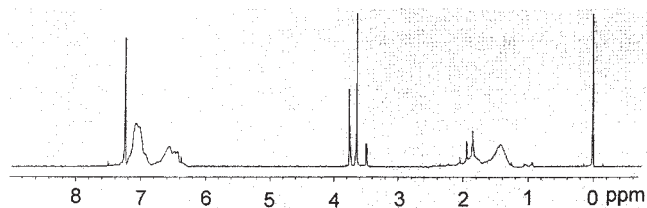


Figure 1 $^1\text{H-NMR}$ spectra of PS-*b*-PEO2000-*b*-PS.

permeation chromatographs (GPC) were obtained on a Waters 1515 instrument (Waters Corp., Milford, MA) at 25°C with THF as eluent at a flow rate of 1 mL/min, using polystyrene as standards. Glass-transition temperature was tested by a SDT 2960 Simultaneous DSC-TGA (TA Company, NewCastle, DE). X ray diffraction was carried out with a D/max-3C X diffraction Instrument (Rigaku, Japan).

Synthesis of PS-*b*-PEO-*b*-PS triblock copolymers

General procedure for synthesis of PS-*b*-PEO-*b*-PS triblock copolymers by atom-transfer radical polymerization (ATRP) was similar to the method of Jankova et al.¹ Bulk polymerizations were carried out in a glass tube (diameter 15 mm, length 200 mm) charged with styrene, PEO dibromomacroinitiator, CuBr, bipy in a 100/1/2/4M ratio. The system was degassed three times with nitrogen, then immersed in an oil-bath thermostat at 110°C for 10–20 h. The crude products were dissolved in dichloromethane, filtered, washed with 5% (mass) acetic acid, and precipitated in a large excess of hexanes. The polymers were dried in vacuum at 30°C, then extracted with cyclohexane for three times for possible removal of PS. The residue was extracted with distilled water for three times to remove possible unreacted PEO macroinitiator. The purified products were dried in vacuum at room temperature.

Test of emulsifying properties

Test of emulsifying properties was carried out in a similar way to that mentioned in Ref.² PS-*b*-PEO-*b*-PS triblock copolymer (0.1 g) was dissolved in 15 mL toluene and then added into 35 mL distilled water. After shaken vigorously for 5 min, the mixture was sealed into a 50-mL measuring cylinder and keeping still for 24 h, the volume of the emulsion (called emulsion volume 1) was recorded. The mixture was again shaken vigorously for 5 min, and keeping still for another 24 h, the volume of the emulsion (named emulsion volume 2) was recorded. The emulsifying abilities of PS-*b*-PEO-*b*-PS triblock copolymers were estimated by emulsion volume.

RESULTS AND DISCUSSION

Characterization of PS-*b*-PEO-*b*-PS triblock copolymers

Figure 1 represented the typical $^1\text{H-NMR}$ spectra of PS-*b*-PEO 2000-*b*-PS triblock copolymers. The signal at 3.46–3.78 ppm was for the methylene group of PEO, the peaks at 6.64–7.05 ppm appeared for the phenyl ring protons in PS. $^1\text{H-NMR}$ spectra confirmed the coexistence of the PS chain and the PEO chain in the macromolecular structure.

The single peak of GPC curve of the products shown in Figure 2 indicated that the products could not be the blend of PS homopolymers and PEO homopolymers. If so, the GPC curves should appear as two peaks, one for the PS homopolymers and the other for the PEO homopolymers.

The proofs from $^1\text{H-NMR}$ spectra and GPC elucidated that the obtained products were PS-*b*-PEO-*b*-PS triblock copolymers. The molecular weight and molecular weight distribution of PS-*b*-PEO-*b*-PS triblock copolymers are listed in Table I.

Thermal character of triblock copolymers

Figure 3 shows DSC curves of PS-*b*-PEO2000-*b*-PS triblock copolymers. It indicated that each triblock copolymer had a single T_g . The T_g s increased from 65.67°C to 88.65°C when the molecular weight of copolymers increased from 4093 to 9916, as shown in Table I. It was obvious that the more PS the triblock copolymer contained, the higher its T_g was, but the T_g of all triblock copolymers was less than that of random PS homopolymers.

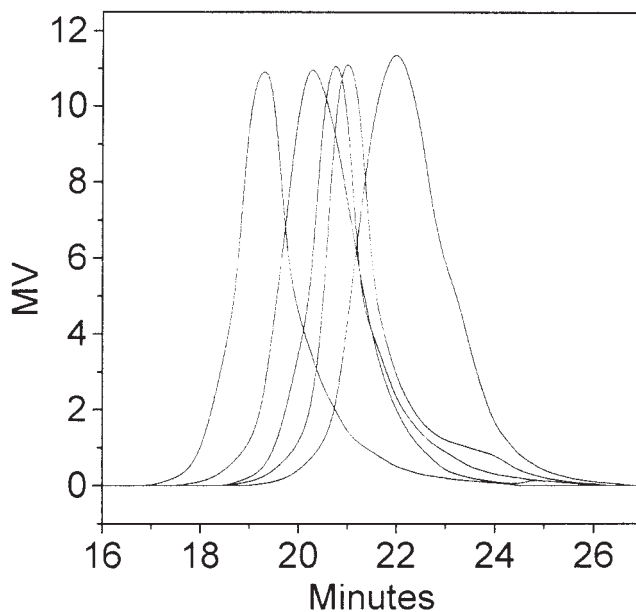


Figure 2 GPC curves of PS-*b*-PEO2000-*b*-PS.

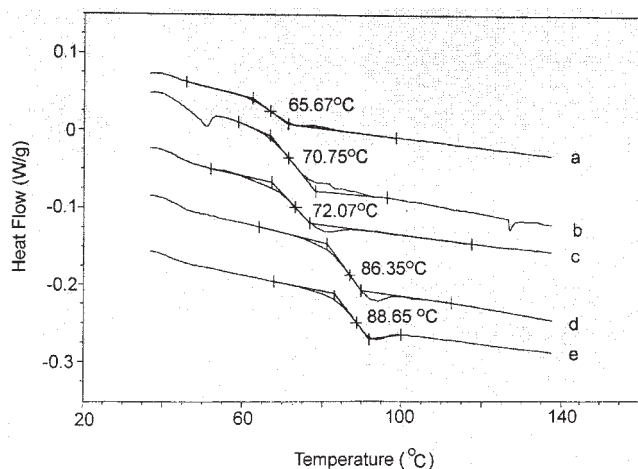


Figure 3 DSC curves of PS-*b*-PEO2000-*b*-PS copolymers a, b, c, d, e.

Crystallinity of triblock copolymers

Figure 4 exhibits diffraction intensity of PEO 2000 homopolymer and PS-*b*-PEO-*b*-PS triblock copolymers at different Bragg diffraction angle (2θ). Firstly, it could be seen that PEO 2000 homopolymer had two very narrow and strong diffraction peaks, while PS-*b*-PEO-*b*-PS triblock copolymers had two broad and weak diffraction peaks, which indicated crystallinity of PS-*b*-PEO-*b*-PS triblock copolymers being notably less than that of PEO 2000 homopolymer. The results can be explained that random PS chains not only cannot crystallize themselves, but also disturb crystallizing of PEO. Secondly, when the molecular weight of copolymers increased, diffraction peaks of copolymers weakened gradually, which indicated that crystallinity of copolymers decreases.

Emulsifying properties of triblock copolymers

After the first 5-min vigorous shaking and keeping still, the copolymer-toluene-water systems separated into three layers, the transparent upper and lower layers were toluene and water, respectively, the middle layer was a milk-white emulsion whose volume shrank gradually during the course of standstill. After

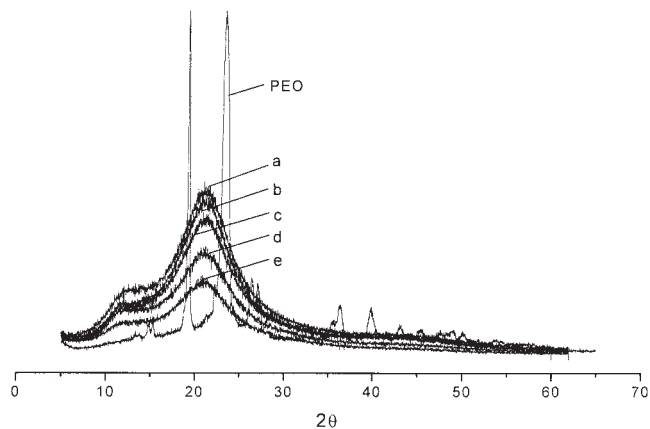


Figure 4 Curves of X-ray diffraction of PEO and copolymers a, b, c, d, e.

24 h, the emulsion volumes of systems containing different copolymers (emulsion volume 1) were recorded (Table II). It was observed that emulsion volume 1 decreased with the increasing molecular weight of PS-*b*-PEO-*b*-PS. It can be explained that a molecule must keep a certain balance of hydrophilic and lipophilic blocks in its structure to be well-amphiphilic, however, the ratio of hydrophilic PEO block becomes less when the molecular weight of PS-PEO2000-PS goes larger, leading to amphiphathy of the triblock copolymer molecules getting worse.

However, when the systems were shaken for 5 min again and keeping still, they became only two layers, the upper transparent toluene layer and the lower milk-white emulsion layer, the emulsion volumes of different copolymer systems (emulsion volume 2) only slightly descended with the ascending molecular weight of PS-*b*-PEO-*b*-PS, as shown in Table II. It could be interpreted that in the former emulsions because the triblock copolymer molecules were dissolved in toluene at the beginning, the PS chains were well swollen while the PEO chains were seriously folded, which was beneficial to water-in-oil emulsion and micelles with PEO as the core and PS as the shell formed. However, these water-in-oil emulsions and the micelles were unstable. After the first 24-h standstill, the PEO chains were swollen by water inside the micelles,

TABLE I
Molecular Weight and Molecular Weight Distribution of PS-*b*-PEO-*b*-PS

No. of PS-PEO2000-PS	M_n (GPC)	Polydispersity	T_g (°C)
a	4093	1.37	65.67
b	5899	1.58	70.75
c	7564	1.39	72.07
d	8839	1.39	86.35
e	9916	1.56	88.65

TABLE II
Emulsion Volumes in Copolymer-Toluene-Water System

No. of PS-PEO2000-PS	Emulsion volume 1 (ml)	Emulsion volume 2 (ml)
a	14	37
b	12	36.5
c	11.2	36
d	10.5	35
e	8.5	34.5

with the aid of shaking, the swollen copolymer molecules in water-in-oil emulsion changed their conformation and moved into water, leading to the formation of micelles with PS as the core and PEO as the shell, and oil-in-water emulsions were produced. The latter emulsions were very stable so that no visible variation could be observed after keeping still for 3 months. This results is consistent with what has been described by Shiyuan Cheng et al.,⁸ that is, when the PS chain and the PEO chain coexisted in a macromolecular chain in water, they could produce micelles with PS as the core and PEO as the shell.

CONCLUSIONS

Well-defined PS-*b*-PEO-*b*-PS triblock copolymers with continuously variable T_g s, crystallinity, and emulsifying abilities have been synthesized by ATRP by controlling molecular weight of copolymers. The T_g of copolymers increased while crystallinity of copolymers decreased gradually when molecular weight of copolymers increased. PS-*b*-PEO-*b*-PS copolymers were amphiphilic and could produce micelles in toluene-water system (volume ratio was 15:35) with PS as the core and PEO as the shell to form stable oil-in-

water emulsions even if mass content of hydrophilic PEO in copolymers was low (the lowest value was 20.2%). The emulsifying abilities slightly dropped when the molecular weight of copolymers rose.

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