

# Facile Method for the Synthesis of Polystyrene–Poly(ethylene glycol) Block Copolymers

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**ABSTRACT:** A facile method for synthesis of polystyrene–poly(ethylene glycol) block copolymers under mild conditions, for instance, ambient temperature and atmospheric pressure, by the direct esterification condensation reaction was developed. The block copolymers were characterized with such techniques as Fourier transform infrared spectroscopy,  $^1\text{H-NMR}$ , gel permeation chromatography, differential scanning calorimetry, and X-ray diffraction. The results show that block copolymers with a yield of over 80%

were successfully synthesized with this facile approach, and the resulting block copolymers exhibited both glass-transition and melting endothermal signals and both amorphous and crystal phases as well; this indicated that the block copolymers had a microphase-separated structure. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 259–265, 2010

**Key words:** block copolymers; esterification; polycondensation; polystyrene; synthesis

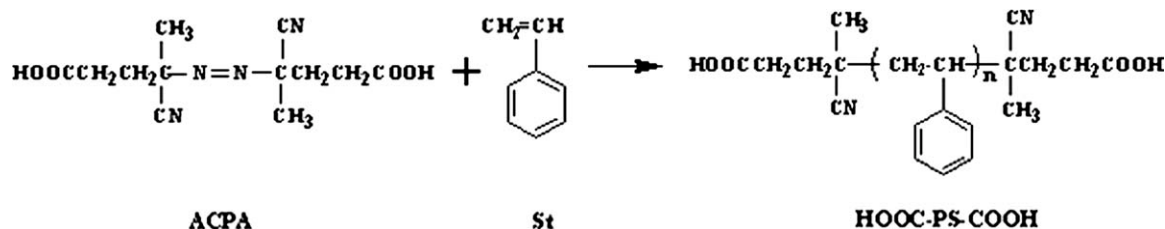
## INTRODUCTION

Amphiphilic block copolymers are of considerable interest for various applications in which the combination of both hydrophilic and hydrophobic properties of these materials may be used, for example, as emulsifiers,<sup>1</sup> dispersion stabilizers and compatibilizers,<sup>2,3</sup> crystallization modifiers,<sup>4</sup> and templates for metal colloids,<sup>5</sup> and polystyrene (PS)–poly(ethylene glycol) (PEG) block copolymers are one of the most frequently used amphiphilic block copolymers; they contain both PS and PEG domains with a microphase-separated structure, which allows the system to exhibit many of the often desirable properties of both components. PS is an important thermoplastic material with excellent transparency, high electrical resistibility, and hydrolytic stability,<sup>6</sup> whereas PEG is regarded as the most effective polymer for reducing protein adsorption and denaturation because of its low interfacial energy, nonadhesion properties, and high dynamic motion.<sup>7,8</sup> To realize these applications, considerable efforts have been made to prepare PS–PEG block copolymers with various approaches, such as (1) traditional free-radical polymerization with a macroinitiator technique,<sup>9</sup> (2) living anionic polymerization,<sup>10</sup> (3) nitroxide-mediated

radical polymerization,<sup>11</sup> (4) atom transfer radical polymerization,<sup>12</sup> and (5) condensation reaction. Among these polymerization methods, block copolymers obtained with the traditional free-radical polymerization method have a broad molecular weight distribution, whereas anionic polymerization has to be carried out under anhydrous conditions, and extensive purification of the monomers, solvents, and initiators is also required, and the choice of monomers is still limited for living radical polymerization (including nitroxide-mediated radical polymerization and atom transfer radical polymerization). As far as the method of the condensation reaction is concerned, the use of the esterification reaction is one of the condensation routes for synthesizing the copolymers. However, it is very difficult to synthesize block copolymers with a high molecular weight because of the low equilibrium constant ( $K$ ) of the esterification reaction ( $K \approx 4$ ).<sup>13</sup> To increase the conversion rate of the monomers and the degree of polymerization in esterification condensation, several means have been adopted, for instance, vacuumization, heating, blasting inert gases,<sup>14</sup> and resorting the intermediate agent, such as  $\text{PCl}_5$  or thionyl chloride, through the procedure of Smith<sup>15</sup> and Ueda et al.<sup>16</sup> As a result, the polymerization process becomes rigorous and complicated. Fortunately, a facile, one-step esterification reaction method,<sup>17</sup> which can be carried out under ambient temperature and moisture, was developed by our research group, and several copolymers<sup>18,19</sup> have been synthesized with this facile method. By using this novel synthetic method and combining the condensation reaction, one can prepare multicomponent

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Scheme 1 Schematic representation for the synthesis of PS-COOH.

polymers under mild conditions. In this article, we present a facile method for synthesizing PS-PEG block copolymers under mild conditions via the direct esterification condensation reaction between PEG and carboxyl-terminated polystyrene (PS-COOH) with dicyclohexylcarbodiimide (DCC) as an activating agent and 4-(dimethylamino) pyridinium-*p*-toluenesulfonate (DPTS) as a catalyst.

## EXPERIMENTAL

### Materials

PEG (PEG600, PEG2000, and PEG10,000, where the numbers following PEG represent number-average molecular weights ( $M_n$ 's) of 600, 2000, and 10,000 g/mol, respectively) was the product of BASF Co. (Shanghai, China) Styrene (St), purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China), was treated with 5 wt % aqueous NaOH to remove the inhibitor, dried over anhydrous calcium chloride, and then stored at a low temperature before use. 4,4'-Azobis-4-cyanopentanoic acid (ACPA) was from Aldrich (Riedstr, Yugoslavia) and was freeze-dried *in vacuo* for 48 h with liquid nitrogen as a cooling agent before use. DPTS was prepared with 4-(dimethylamino) pyridine and *p*-toluenesulfonic acid according to the method described in ref. 17. DCC, 1,4-dioxane, tetrahydrofuran (THF), ethyl ether, *N,N'*-dimethylformamide (DMF), and methanol were all from Sinopharm Group Chemical Reagent Co. and were used as received.

### Synthesis of PS-COOH

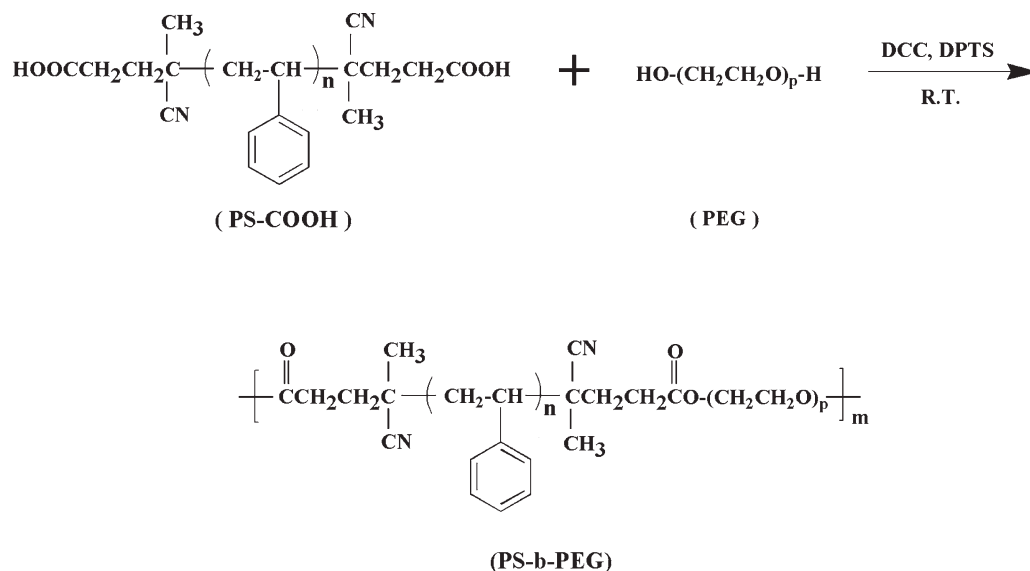
PS-COOH was synthesized by the use of ACPA as the functional initiator and St as the monomer. The polymerization of St was carried out in a 250-mL, four-necked flask equipped with a mechanical stirrer, an  $N_2$  inlet, a thermometer with a temperature controller, a Graham condenser, and a heating mantle with the following process: first, 96 mmol (10 g) of St was dissolved in 40 g of 1,4-dioxane in the flask; this was then heated to 50°C and kept at that temperature for 0.5 h under stirring with the protection of nitrogen. After 0.36 mmol (0.1 g) of ACPA was charged to the flask, the polymerization reaction was carried out at 75°C for 6 h. The resulting mix-

ture was isolated by slow precipitation with methanol and filtered. After it was dried *in vacuo* at 40°C for 12 h, the product, with a yield of 82.0 wt %, was obtained.

The schematic process for the synthesis of the PS-COOH is described in Scheme 1. As the free-radical polymerization of St over 60°C was terminated principally by recombination, a dominating PS with two terminal carboxylic acids was obtained, just as described in Scheme 1. Of course, a very small amount of PS with one terminal carboxylic acid could also be engendered because of the unavoidable disproportionation termination. Therefore, the structure of the resulting PS in Scheme 1 is just an approximation.

### Synthesis of the PS-PEG block copolymers

PS-PEG block copolymers were prepared via the direct one-step esterification condensation reaction between PS-COOH and PEG by the use of DCC as an activating agent and DPTS as a catalyst under mild conditions, that is, ambient temperature and atmospheric pressure. PS-PEG block copolymers were synthesized according to the following procedure: PEG (1.0 mmol; the weights for PEG600, PEG2000, and PEG10,000 were 0.60, 2.0, and 10.0 g, respectively), PS-COOH (1.0 mmol, 18.7 g), and DPTS (0.4 mmol, 0.118 g) were charged into a 250-mL, round-bottom flask containing a mixture of THF and DMF (the quantity of the mixture was three times the total amount of PEG, PS-COOH, DCC, and DPTS). After all of the solutes were dissolved, a DCC solution (3.0 mmol, 0.619 g) dissolved in one fourth the total amount of THF) was charged and stirred at room temperature for 24 h. The resulting viscous suspension was filtered to remove the formed dicyclohexylurea, which was rinsed with THF three times. Then, the mixture was poured into excess heptane and filtered. After the precipitate was vacuum-dried at 40°C for 10 h, the resulting product was extracted with ethyl ether three times by a liquid-liquid extraction method to remove the unreacted PS-COOH and with deionized water three times to remove the unreacted PEG. Then, the product was dried *in vacuo* again at 40°C to a constant weight. The final obtained product was a white powder with a yield of 80–85 wt %, which was



**Scheme 2** Schematic representation for the synthesis of the PS-PEG block copolymers (where R.T. denotes the room temperature).

designated as  $gyx$ , where  $x$  denotes the block copolymers synthesized from PEG with different molecular weights; namely,  $gy01$ ,  $gy02$ , and  $gy03$  were prepared from PEGs with  $M_n$ 's of 600, 2000, and 10,000 g/mol, respectively. The schematic process for the synthesis of the block copolymers is described in Scheme 2.

### Characterization

#### Fourier transform infrared (FTIR) analysis

FTIR spectroscopy was done with a VERTEX 70 FTIR spectrometer (Bruker, Karlsruhe, Germany), and the KBr pellet technique was adopted.

#### <sup>1</sup>H-NMR analysis

<sup>1</sup>H-NMR spectra were recorded on an AVANCE DRX-300 spectrometer (Bruker, Karlsruhe, Germany) with CDCl<sub>3</sub> as the solvent and tetramethylsilane as the internal standard.

#### Gel permeation chromatography (GPC) measurement

The molecular weight and its distribution were measured by GPC (PL-50, Polymer Lab, Church Stretton, United Kingdom). THF was used as the eluant, and narrow PS as was used as the calibration standard.

#### Differential scanning calorimetry (DSC) measurement

DSC measurements were conducted on a Shimadzu DSC-60 (Kyoto, Japan) instrument calibrated with in-

dium and *n*-octane. A sample with a weight of about 10 mg was heated from about 30 to 150°C at a heating rate of 20°C/min. The glass-transition temperature ( $T_g$ ) was determined from the midpoint of the change in the heat capacity.

#### X-ray diffraction (XRD)

Crystal structure identification was carried out with a Shimadzu XRD-7000LX XRD meter with Cu K $\alpha$  irradiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a scanning rate of 0.02°/s at  $2\theta$  values ranging from 10 to 80°.

## RESULTS AND DISCUSSION

### Synthesis and characterization of PS-COOH

PS-COOH was synthesized with ACPA as the functional initiator to initiate the polymerization of St through the free-radical polymerization method. The final resulting product was characterized by the <sup>1</sup>H-NMR and FTIR techniques, as shown in Figures 1 and 2(b), respectively.

The <sup>1</sup>H-NMR spectrum of the resulting product (Fig. 1) showed the appearance of the proton peaks in the phenyl ring at 6.4–7.1 ppm, whereas the peaks at about 1.4 and 1.9 ppm were attributed to methylene and hypomethyl protons, respectively. The carboxyl proton was not observed in the <sup>1</sup>H-NMR spectrum because the carboxyl groups only existed at the end of the polymer chains, and the polymer chain was very long. The IR absorbance of the carbonyl groups moved from 1720 cm<sup>-1</sup> in ACPA [Fig. 2(a)] to 1740 cm<sup>-1</sup> in the product [Fig. 2(b)], whereas the absorbance peak of -CN at about 2240 cm<sup>-1</sup> was not be observed because of the small amount of

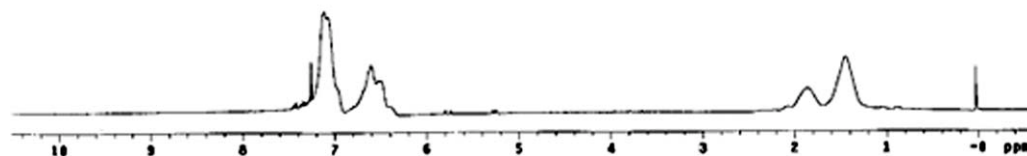


Figure 1  $^1\text{H-NMR}$  spectrum of PS-COOH.

—CN groups in PS-COOH. Meanwhile, the peaks at  $1450\text{--}1600\text{ cm}^{-1}$  were assigned to phenyl-ring vibrations. In addition, the wide absorption bands at  $2850\text{--}3150\text{ cm}^{-1}$ , attributed to both methylene and hydrogen bonds, were observed in the FTIR spectrum, which further proved that hydroxyl groups were present in the resulting product. Combining the characterization results from  $^1\text{H-NMR}$  and FTIR, we concluded that PS-COOH was successfully synthesized. The  $M_n$  and the molecular weight distribution of the resulting PS-COOH, determined by GPC, were 18,700 and 1.39, respectively.

#### Synthesis and characterization of the PS-PEG block copolymers

The PS-PEG block copolymers were synthesized via a facile one-step condensation method via the esterification reaction between PS-COOH and PEG under mild conditions.

The key factor for the successful synthesis of the PS-PEG block copolymers was the solvent selection for PS, which is a hydrophobic polymer, and PEG, which is a hydrophilic polymer; therefore, a solvent that could dissolve both PS and PEG needed to be chosen, and meanwhile, the selected solvent also needed good dissolving ability for the DCC (used as the activating agent) and DPTS (used as the cata-

lyst). At the very start, THF was adopted as the solvent for the synthesis of the block copolymers, however, the yield of the resulting copolymers was very low (ca. 30%) because the solubility of DPTS was poor in THF at room temperature. To solve this problem, some DMF was then used together with the THF because DMF was a good solvent for DPTS, but the composition of the solvent mixture was very critical because of the poor solubility of PS and DCC in DMF. Our experiments showed that a homogeneous solution could be obtained when the solvent mixture was at a weight ratio of 1 : 5 DMF to THF. At this point, the yield of the copolymers was over 80%.

The successful synthesis of the PS-PEG block copolymers was confirmed by the FTIR and  $^1\text{H-NMR}$  spectra, as shown in Figures 2(d) and 3. For the sake of comparison, the FTIR spectrum of PEG is also presented in Figure 2(c).

Compared to the FTIR spectrum of PS-COOH [Fig. 2(b)], the spectrum of the resulting copolymers [Fig. 2(d)] also showed the appearance of the characteristic stretching vibration peaks for the phenyl-ring framework at  $1450\text{--}1500$  and  $1580\text{--}1600\text{ cm}^{-1}$  and for the single-replaced phenyl ring at  $690\text{--}710$  and  $730\text{--}770\text{ cm}^{-1}$ , respectively. Meanwhile, a new strong peak between  $1020$  and  $1150\text{ cm}^{-1}$  for C—O—C stretching vibrations from PEG chains was observed. In addition, as compared to the FTIR spectrum of PEG [Fig. 2(c)], the absorption at  $1740\text{ cm}^{-1}$  due to  $\nu_{\text{CO}}$  and the absorption bands of the phenyl ring from the PS-COOH chains at  $1450\text{--}1500$  and  $1580\text{--}1600\text{ cm}^{-1}$  were present in the FTIR spectrum of the PS-PEG block copolymers. On the other hand, the proton signals of the phenyl ring at  $6.4\text{--}7.1$  ppm and the methylene and hypomethyl proton peaks at  $1.45\text{--}1.95$  ppm from the PS chains were observed in the  $^1\text{H-NMR}$  spectrum of the gy03 PS-PEG block copolymers (Fig. 3). Simultaneously, the proton peak at  $3.5\text{--}3.8$  ppm from —OCH<sub>2</sub>CH<sub>2</sub>— groups in the PEG chains is shown in Figure 3. Therefore, the  $^1\text{H-NMR}$  spectrum provided strong evidence for the presence of both PEG and PS segments in the copolymer chain.

All of these results show that both PS and PEG chains were detected in the resulting copolymers, whereas the unreacted PS-COOH and PEG were removed by the extraction of ethyl ether and deionized water, respectively. So, the results from FTIR

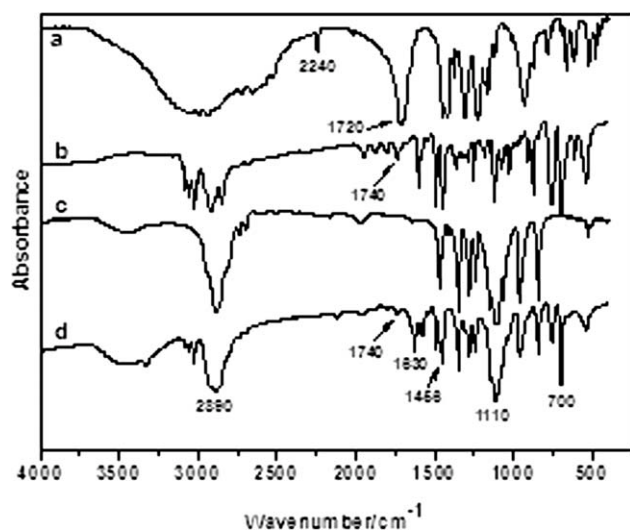
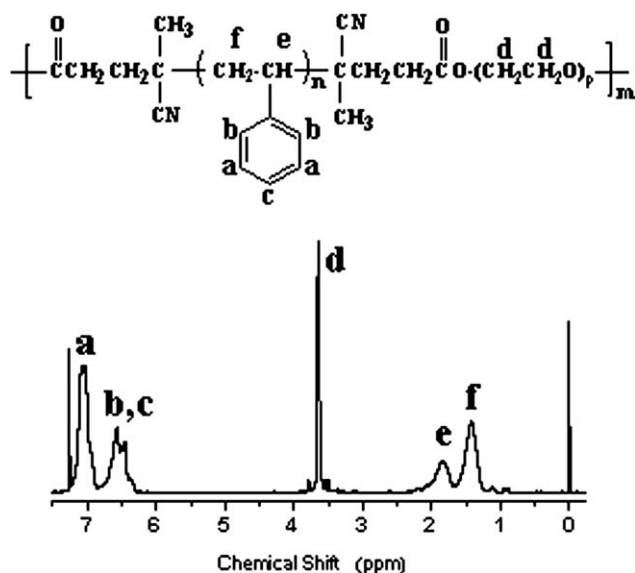


Figure 2 FTIR spectra for (a) ACPA, (b) PS-COOH, (c) PEG, and (d) PS-PEG copolymers.



**Figure 3** Typical  $^1\text{H-NMR}$  spectrum of the PS-PEG block copolymers (gy03).

and  $^1\text{H-NMR}$  spectroscopy demonstrated that the resulting copolymers were composed of PS and PEG segments. Therefore, we concluded that the condensation reaction between PS-COOH and PEG took place effectively under mild conditions, that is, ambient temperature and atmospheric pressure, and the PS-PEG block copolymers were synthesized successfully.

The composition of PS-PEG block copolymers were calculated by the areas ratio of the protons in the phenyl ring and  $-\text{OCH}_2\text{CH}_2-$  from  $^1\text{H-NMR}$  according to the following equation:

$$\frac{x}{y} = \frac{S_0/5}{S_1/4} \quad (1)$$

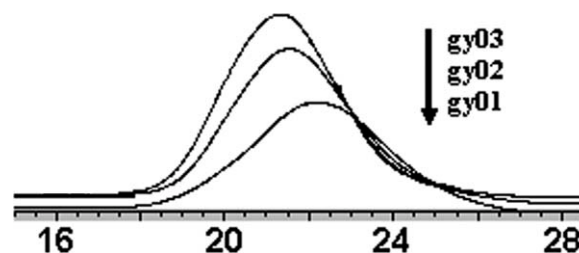
where  $x$  and  $y$  are the number of moles of the monomer units PS and PEG, respectively, and  $S_0$  and  $S_1$  are the total areas of the proton peaks in the phenyl ring and  $-\text{OCH}_2\text{CH}_2-$  groups, respectively. The molar content of PS repeat units in the resulting copolymers is summarized in Table I. The incorporated amount of PS was close to the charged amount; this indicated a high efficiency of the syn-

**TABLE I**  
Characteristics of the PS-PEG Block Copolymers

Block copolymer	PS repeat unit (mol %)		Molecular weight <sup>b</sup>	
	Feed	Copolymer <sup>a</sup>	$M_n$	$M_w/M_n$
gy01	93.0	95.3	78,400	1.76
gy02	79.9	81.2	83,500	1.88
gy03	44.2	45.3	87,200	1.96

<sup>a</sup> Determined by  $^1\text{H-NMR}$ .

<sup>b</sup> Determined by GPC.



**Figure 4** GPC curves of the block copolymers.

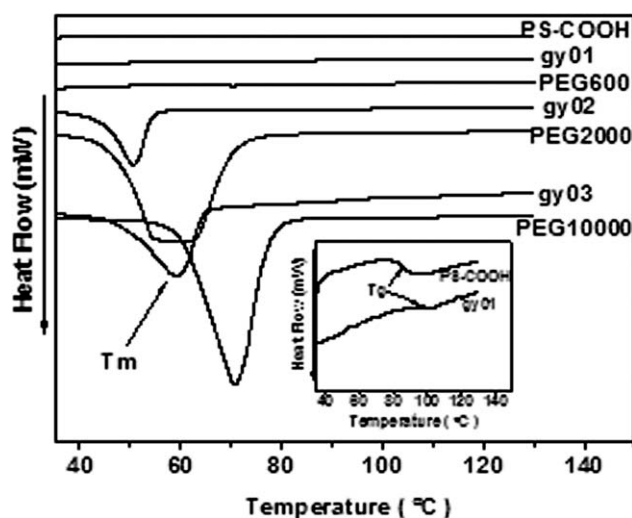
thesis route.

The crude PS-PEG block copolymers were purified with the alternate extraction method with deionized water and ethyl ether. The efficiency of the purification by extraction was proven by the GPC curves for all of the block copolymers (Fig. 4). Only one peak without a shoulder was observed for the curves after purification; this further confirmed that there was no unreacted PEG or PS-COOH in the final purified copolymers.

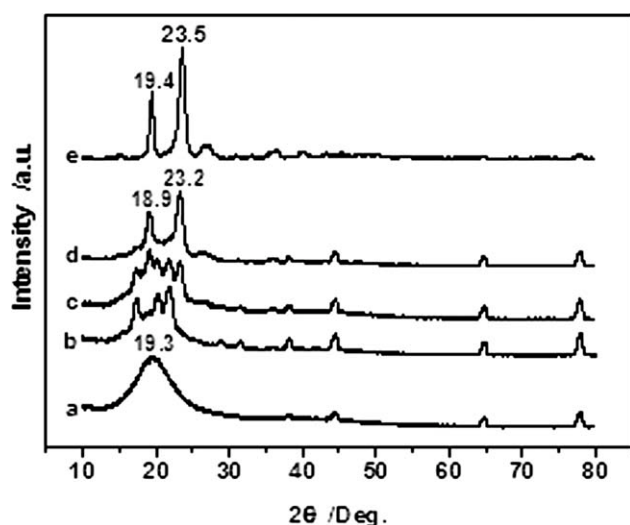
$M_n$  and its polydispersity index [weight-average molecular weight ( $M_w$ )/ $M_n$ ] are also given in Table I. The resulting copolymers had high molecular weights, and the molecular weight distributions for all of the block copolymers were relatively narrow.

#### Thermal analysis of the PS-PEG block copolymers

The thermal properties of the obtained block copolymers (gy01, gy02, and gy03), together with those of PS-COOH and PEG, were characterized by DSC, and the corresponding curves are shown in Figure 5. The DSC traces of gy02, gy03, PEG2000, and PEG10,000 exhibited endothermic peaks that should have been caused by the melting of semicrystalline PEG domains. Furthermore, the melting points



**Figure 5** DSC traces of the PS-COOH, PEG600, PEG2000, PEG10,000, and block copolymers (gy01, gy02, and gy03).



**Figure 6** XRD traces of (a) PS-COOH, the block copolymers [(b) gy01, (c) gy02, and (d) gy03], and (e) PEG.

( $T_m$ 's) of PEG were lower than those of the corresponding copolymers. For example, the  $T_m$  values of PEG2000 and PEG10,000 were 61 and 71°C, whereas the  $T_m$  values of gy02 and gy03 were 51 and 59°C, respectively. By contrast, melting endothermal peaks of PEG600 and gy01 were not observed because of the low molecular weight and the less crystal part of PEG600. Thus, we found that the crystal extent of the PEG domains in the block copolymers increased with increasing molecular weight of PEG.

Glass transitions were also observed for samples PS-COOH and gy01, as shown in the magnified DSC traces, and correspondingly, their  $T_g$ 's were 86 and 97°C, respectively, which resulted from the transition of the PS segments from the glass state to the rubbery state. However, the glass transitions of copolymers gy02 and gy03 were not discernable, which may have been because the PEG crystals restrained the free movements of the PS chains because the molecular weight of PEG in these copolymers was quite large. The existence of the individual thermal signatures of both PS and PEG phases revealed that microphase separation between the PS and PEG domains in the block copolymers occurred; this was also observed in PS-PEG graft and block copolymers.<sup>6,20</sup>

### Crystallization of the PS-PEG block copolymers

The crystal structure of the obtained block copolymers (gy01, gy02, and gy03), together with those of PS-COOH and PEG ( $M_n = 10,000$  g/mol), were investigated by XRD, and the corresponding testing traces are shown in Figure 6. The XRD trace of PS-COOH indicated that the PS-COOH existed in an amorphous phase at room temperature because of a broad peak present at  $2\theta = 19.3^\circ$ , whereas PEG

( $M_n = 10,000$  g/mol) existed in a crystal phase because two distinct crystal peaks were present in the XRD trace of PEG at  $2\theta = 19.4$  and  $23.5^\circ$ , respectively, which indicated that the crystal structure of PEG was monoclinic.<sup>21</sup> By contrast, the amorphous peak of the PS domain and the crystal peaks of the PEG domain overlapped in the XRD traces of the block copolymers (traces b, c, and d in Fig. 6); that is, both the amorphous peak of PS and the crystal peaks of PEG were present in the XRD traces of the block copolymers. Furthermore, new peaks were present in the XRD traces of gy01 and gy02 that were probably due to the PEG domains of different crystallinities, that is, the crystallinities of the localized PEG domains and the domains of PEG in the PS-PEG phase continuum, which resulted from the low molecular weight of PEG and the influence of the condensed state of PS segments. Frey et al.<sup>22</sup> observed multiple transitions for esterified hyperbranched polyether polyols, which were believed to result from different crystallites, and Wooley et al. also observed multiple transitions for PEG-containing hyperbranched polymers.<sup>23</sup> Therefore, we found that the molecular weight of PEG had a strong influence on the crystallinity of the copolymers, as the peak shape of the copolymers gradually developed from amorphous to crystal with increasing molecular weight of PEG, and the PEG crystals nearly possessed the same crystal structure as the pure PEG when  $M_n$  of PEG reached 10,000 (for copolymer gy03).

## CONCLUSIONS

A kind of amphiphilic block copolymer containing PS and PEG segments was successfully synthesized by a direct, one-step esterification condensation reaction by the use of DCC as an activating agent and DPTS as a catalyst under ambient temperature and atmospheric pressure; the synthetic approach was quite facile, and the synthetic conditions were mild compared to those of the conventional method for the preparation of block copolymers by the esterification method. The facile synthetic method is expected to extend to the synthesis of other block copolymers via the direct condensation reaction between different hydroxyl-terminated polymers and carboxyl-terminated polymers.

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