

Synthesis and Surface Properties of Polystyrene-graft-poly(ethylene glycol) Copolymers

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ABSTRACT: Polystyrene-graft-poly(ethylene glycol) copolymers (PS-g-PEG) were successfully synthesized using the "grafting-through" method. The graft copolymers and the surface properties of their coats were characterized by ¹H-NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), static contact angle measurement, and atomic force microscopy (AFM). Both DSC and TEM indicated that the graft copolymers had a microphase separated

structure. AFM showed the microphase separated structure also occurred at the coat surface, especially at high PEG content, which could also be indirectly confirmed by the XPS and contact angle results. The formation mechanism of the microphase separated structure was discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1458–1465, 2007

Key words: microphase separation; polystyrene-graft-poly(ethylene glycol); surface properties

INTRODUCTION

Of increasing interest is how to control the microstructure and morphology of the surface of materials at the nanometer and submicrometer scale, since it is hypothesized that materials exhibiting nanoscopically resolved morphological and topographical surfaces will be capable of inhibiting protein adsorption; consequently, they can be used as biocompatible and antifouling materials.^{1–3} Copolymers consisting of chemically distinct polymeric segments undergoing microphase separation as a result of enthalpically driven segregation have led to a remarkable range of nanostructured morphologies, such as spherical, cylindrical, lamellar, and gyroidal phase.^{4,5} Thus, copolymers with a microphase separated structure are ideal materials for biocompatible or antifouling applications. The most frequently studied copolymers with a microphase separated structure are block copolymers. Graft copolymers are also expected to exhibit a microphase separated morphology that was theoretically deduced by the Flory-Huggins theory and mean field theory^{6,7} and experimentally demonstrated in the graft copolymers of palmitate-graft-poly(vinyl alcohol)⁸ and poly

(vinyl alcohol)-graft-polystyrene.⁹ However, the microphase separated morphology of other graft copolymers are seldom reported because of the difficulty in synthesizing the graft copolymers with a well-defined molecular architecture.¹⁰

Our interests are focused on poly(ethylene glycol) (PEG)-containing polymers since PEG is well-known for its extraordinary ability to resist protein adsorption, which is believed to result from its hydrophilicity, large excluded volume, and unique coordination with surrounding water molecules in an aqueous medium.^{11–13} It is usually used as one of the segments in biocompatible and antifouling polymers. However, most of the PEG-containing polymers studied are block copolymers or polymer blends,^{14,15} while the PEG-containing graft copolymers reported mainly focus on their amphiphilicity and serve as emulsifiers, surfactants, surface modifiers, and so on.¹⁶ Very little research is involved in the microphase separated behavior of PEG-containing graft copolymers. On the other hand, PEG is a semicrystalline polymer and can organize both on a very local scale (crystallization) and on a mesoscopic scale (microphase separation), so diverse and interesting surface morphologies, and thus various coat surface properties of PEG-containing graft copolymers would be expected. Therefore, the graft copolymers containing PEG side chains were designed and synthesized through copolymerizing styrene with poly(ethylene glycol monomethacrylate) (PEGMA) macromonomer in this study. The surface composition, surface morphology, and surface wetting properties of the graft copolymer coats were investigated in detail.

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EXPERIMENTAL

Materials

Poly(ethylene glycol) monomethyl ether (MPEG, $M_n = 5000$ g/mol) is a product of Fluka (Buchs, Switzerland) and was dehydrated by a short-path distiller before use. Styrene (St) and toluene were purchased from Sinopharm Group Chemical Reagent (Shanghai, China) and the former was treated with aqueous NaOH to remove the inhibitor; both were dried over anhydrous CaCl_2 . Triethylamine (NEt_3) was also from Sinopharm Chemical. Methacryloyl chloride (MAC) was obtained from Aldrich (Milwaukee, WI). Azobisisobutyronitrile (AIBN) was recrystallized from ethanol before use. Other reagents were used as received.

Synthesis of PEGMA macromonomer

The PEGMA macromonomer was synthesized through an end-group exchange reaction of MPEG with MAC using NEt_3 as the catalyst and toluene as the solvent according to the following procedure: 100 g MPEG and 4.18 g NEt_3 were first dissolved in 300 g toluene in a 500-mL four-necked flask at room temperature. Then 4.05 g MAC dissolved in 10 g toluene was added dropwise to the solution over 0.5 h under a nitrogen atmosphere and vigorous stirring. After the addition, the mixture was reacted at room temperature for 2 h and then gradually heated to 45°C over 0.5 h and continuously reacted at that temperature for another 24 h. Subsequently, the reactant solution was filtered to remove the precipitate of NEt_3 salt and the filtrate was poured into a large amount of heptane to precipitate the product. The crude product was further dissolved in chloroform and reprecipitated with heptane. This purifying process was repeated three times to remove unreacted MAC. The final product was dried at 40°C under vacuum to constant weight.

Synthesis of PS-g-PEG copolymers

The PS-g-PEG copolymers were prepared with the "grafting-through" method, namely, free radical copolymerization of St and PEGMA macromonomer. The copolymerization was carried out in a 250-mL round-bottom flask equipped with a mechanical stirrer, an N_2 inlet, a thermometer with temperature controller, a Graham condenser, and a heating mantle using the following process: 20 g of total weight of PEGMA and St together with 0.2 g AIBN were first dissolved in 60 g of toluene in the flask, then heated to 70°C and kept at that temperature for 12 h under stirring with the protection of nitrogen. The reaction was terminated with hydroquinone and 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 deionized water

three times to remove the unreacted PEGMA macromonomer and MPEG, then extracted with ethyl ether three times to remove the St homopolymer and vacuum-dried again at 40°C to constant weight. The product finally obtained was a white powder and designated SP $_x$, where x denotes the content of PEG (wt %) in the copolymers.

Preparation of polymer coats

Thin polymer coats for X-ray photoelectron spectroscopy (XPS) and contact angle measurement were cast from the dilute solution of PS-g-PEG in chloroform (0.5 wt %) on clean glass flakes. Thin coats with a thickness of about 60 nm for atomic force microscopy (AFM) observation were spin-coated onto silicon wafers, which were freshly cleaned at 80°C for 20 min in a piranha solution (a mixture of 70 mL of 98% sulfuric acid and 30 mL of 30% H_2O_2 solution), at a speed of 3500 rpm and ambient conditions. Then the coats were placed in vacuum at ambient temperature for 3 days to remove the remaining solvent.

Characterization

The FT-IR spectra were obtained with a Nexus 470 FT-IR spectrometer (Nicolet, Thermo Electron, San Jose, CA).

The molecular weight was measured by gel permeation chromatography (GPC, Waters Breeze 1515, Milford, MA). Tetrahydrofuran (THF) was used as the eluant and narrow polystyrene as the calibration standards.

The copolymer composition was estimated by $^1\text{H-NMR}$ spectra recorded on a VANCE DSX-500 (Bruker, Germany) spectrometer, using CDCl_3 as the solvent and tetramethyl silane (TMS) as internal standard.

Differential scanning calorimetry (DSC) experiments were conducted on an NETZSCH DSC 200 PC (NETZSCH, Germany) under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

Transmission electron microscopy (TEM) was performed on thin films cast from 0.5 wt % copolymer solutions in CHCl_3 on the surface of water. Grids were placed on top of the film and collected from the water surface using a glass slide. Samples (grids with thin films) were vapor-stained with an aqueous solution of 0.5 wt % RuO_4 in glass-covered dishes for 20 min and observed with a transmission electron microscope (H600, Hitachi, Japan).

The surface morphology of the coats was characterized by an atomic force microscope (AFM, SPA300HV, Seiko Instruments, Japan) in ultra-light-tapping mode under ambient conditions. A micro-fabrication cantilever with a constant of ~ 20 N/m and a scan rate of 2 Hz was used.

The surface compositions of the graft copolymer coats were characterized by XPS. The spectra were recorded on a PHI 5000C ESCA System (Perkin Elmer, Norwalk, CT) using Al K α exciting radiation.

Contact angle measurements were performed with the sessile drop technique using OCA15 (Dataphysics Instruments, Germany) at room temperature. The static contact angle (θ_s) of water was measured on the coats at contact time $t = 15$ s after the water drop (2 μ L) application. The reported values were an average of five individual measurements on different regions of the same sample.

RESULTS AND DISCUSSION

Synthesis and characterization of PEGMA macromonomer

The PEGMA macromonomer was prepared through an end-group exchange reaction of MPEG with MAC. The final product was characterized by FT-IR spectrum as shown in Figure 1. For the sake of comparison, the FT-IR spectrum of MPEG was also presented. The new peaks at 1720 cm^{-1} and 1640 cm^{-1} , due to the carbonyl group and double bond, respectively, were observed and meanwhile the peak at about 3500 cm^{-1} assigned to the hydroxyl group decreased greatly, indicating that the PEGMA macromonomer was successfully synthesized. This could also be confirmed by the appearance of methylic protons at 1.9 ppm and vinylic protons at 5.6 ppm and 6.1 ppm in its $^1\text{H-NMR}$ spectrum, as shown in Figure 2(a). Based on the areas ratio of protons between methylic and $-\text{OCH}_3$ groups (3.4 ppm), the end-group functionality of the resulting product was 85%, indicating that the product was actually a mixture of PEGMA macromonomer with a small amount of unreacted MPEG. The number-average

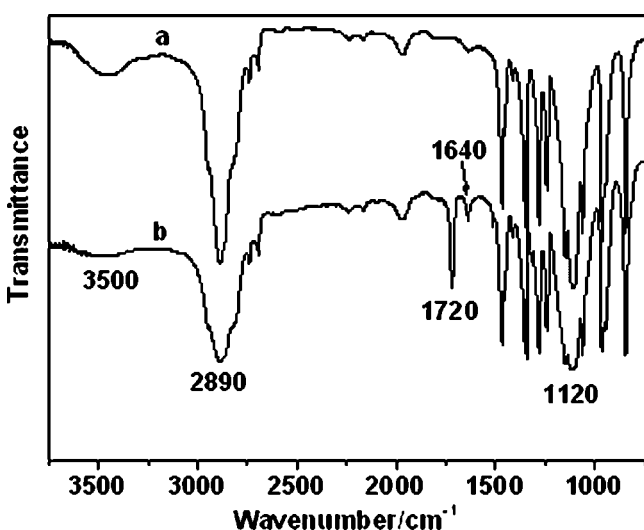


Figure 1 FT-IR spectra for (a) MPEG and (b) PEGMA macromonomer.

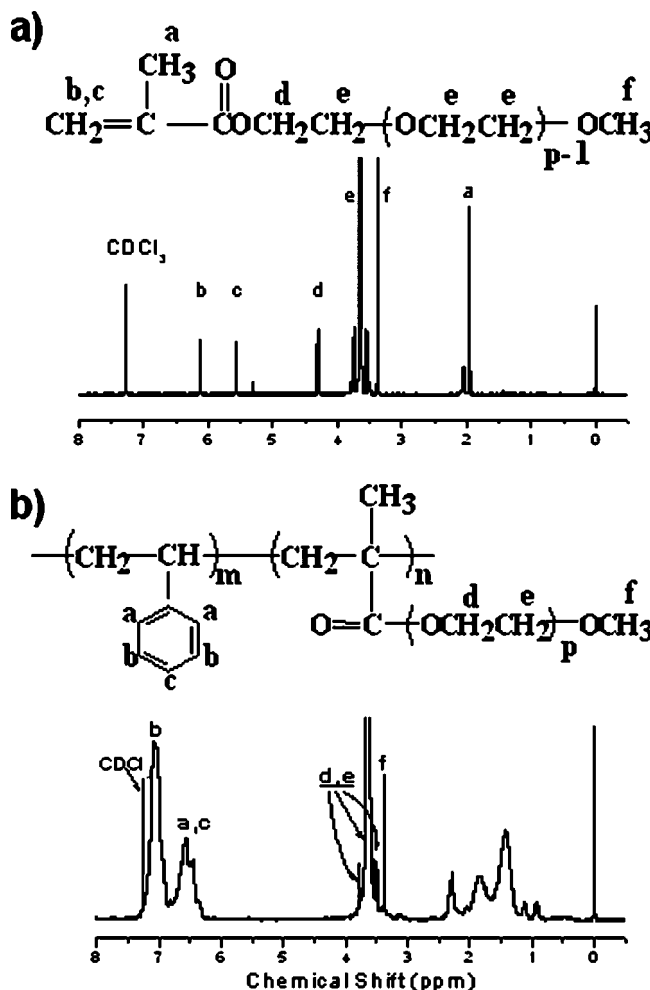
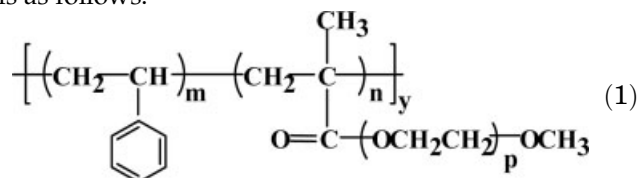


Figure 2 $^1\text{H-NMR}$ spectra of PEGMA macromonomer (a) and the graft copolymer (SP66) (b).

molecular weight and the molecular weight distribution were 5050 and 1.27, respectively.

Synthesis and characterization of PS-g-PEG copolymers

The PS-g-PEG copolymer was synthesized by free radical copolymerization as described in the Experimental section. The structure of the resulting graft copolymer is as follows:



The graft copolymer was characterized by $^1\text{H-NMR}$ spectrum as shown in Figure 2(b). The peaks at 6.4 ~ 7.1 ppm attributed to the protons in the phenyl-ring while the peaks at 3.5~3.8 ppm were due to the protons in $-\text{OCH}_2\text{CH}_2-$ groups, and the single peak at 3.4 ppm was from protons in the $-\text{OCH}_3$ group.

TABLE I
Characteristics of PS-g-PEG Copolymers

Samples	PEGMA contents (wt %) in		Molecular weight and distribution ^c		
	Feeding monomers ^a	Copolymers ^b	M_n	M_w	PDI
SP28	8	28	14410	17571	1.22
SP37	18	37	12528	15865	1.26
SP45	26	45	12629	15069	1.19
SP66	46	66	10023	12284	1.23

^a The accurate PEGMA content and the unreacted MPEG was not included.

^b Calculated by Equation (2) based on the ¹H-NMR spectra.

^c Determined by GPC method.

These results confirmed the actual synthesis of PS-g-PEG copolymer.

The composition of PS-g-PEG graft copolymer could be calculated from the area ratios of protons in the phenyl-ring and -OCH₂CH₂- according to the following equation:

$$\frac{m}{n} = \frac{S_0/5}{S_1/(4p)} \quad (2)$$

where S_0 and S_1 are the total areas of proton peaks in the phenyl-ring and -OCH₂CH₂- groups, respectively, and p is the number of -OCH₂CH₂- repeat unit in a PEG molecule. The weight contents of PEG in feed monomers and graft copolymers are summarized in Table I.

The crude PS-g-PEG copolymers were purified with the alternate extraction method by using deionized water and ethyl ether, respectively. The efficiency of the purification by extraction was proved by the GPC curves (not shown) for all graft copolymers. Only one peak without a shoulder was observed for the curves after purification, confirming that there was no unreacted PEGMA macromonomer, MPEG, and PS homopolymer in the final purified graft copolymers.

The average molecular weight (M_w and M_n) and its polydispersity index are also given in Table I. It was found that the molecular weight distribution for all graft copolymers was relatively narrow and almost accordant.

The PS homopolymer (M_n : 17950 g/mol, M_w/M_n : 1.7), PEG homopolymer (HomoPEG), and the obtained PS-g-PEG copolymers were also characterized by DSC and the corresponding curves are shown in Figure 3. All DSC curves of copolymers and HOMOPEG exhibited endothermic peaks that should be caused by the melting of semicrystalline PEG domains, and the DSC curve of PS exhibited the glass transition (T_g , ~ 97°C). The glass transitions were additionally observed for samples SP28 and SP37, and correspondingly, their T_g 's were 93°C and 78°C, respectively. However, the

glass transitions for samples SP45 and SP66 were not discernable, which might have been concealed by the endothermic peaks. The existence of the individual thermal signatures of PS backbone and PEG side chain revealed that the microphase separation between PS backbone and PEG side chain in the PS-g-PEG copolymer may have occurred, which was also observed in PS-*block*-PEG copolymers.⁴

Figure 3 also shows that the melting points of the PS-g-PEG copolymers increased with the increasing PEG weight percentage and gradually approached the melting point of HOMOPEG (T_m , ~ 66°C), except for sample SP45, which had two melting points, $T_{m,1}$ and $T_{m,2}$, indicating two kinds of crystal domains. The high $T_{m,2}$ may be caused by the crystallinity of the localized PEG domains and the low $T_{m,1}$ by the domains of PEG in the PS-g-PEG phase continuum, resembling the melting of PEG-containing hyperbranched polymer reported by Frey and coworkers¹⁷ and Gudipati et al.¹⁸ In addition, the T_g for PS segments in graft copolymers was lower than that of PS homopolymer (T_g , ~ 97°C), which was also observed in the block copolymer of PS and PEG,⁴ suggesting that the condensed state of PS segments changed as a result of the bonding of PEG segments.

Morphology of PS-g-PEG copolymers

The TEM micrographs of the films of PS-g-PEG copolymers are displayed in Figure 4. The dark regions are the PEG domains, since PEG segments were more easily stained by RuO₄ than PS segments.¹⁹ From the TEM photographs, it was clearly seen that nanoscopic microphase separation took place for all copolymers, agreeing with the DSC results. However, at relatively low PEG content the films changed from a "network" structure (SP28, large domain of PS and thin network of PEG) to an "island-sea" structure (SP37, PS sea, and

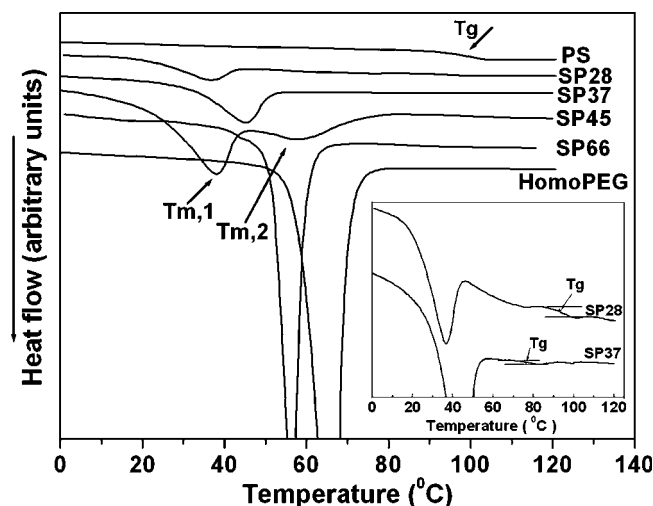


Figure 3 DSC curves of homopolymers and copolymers.

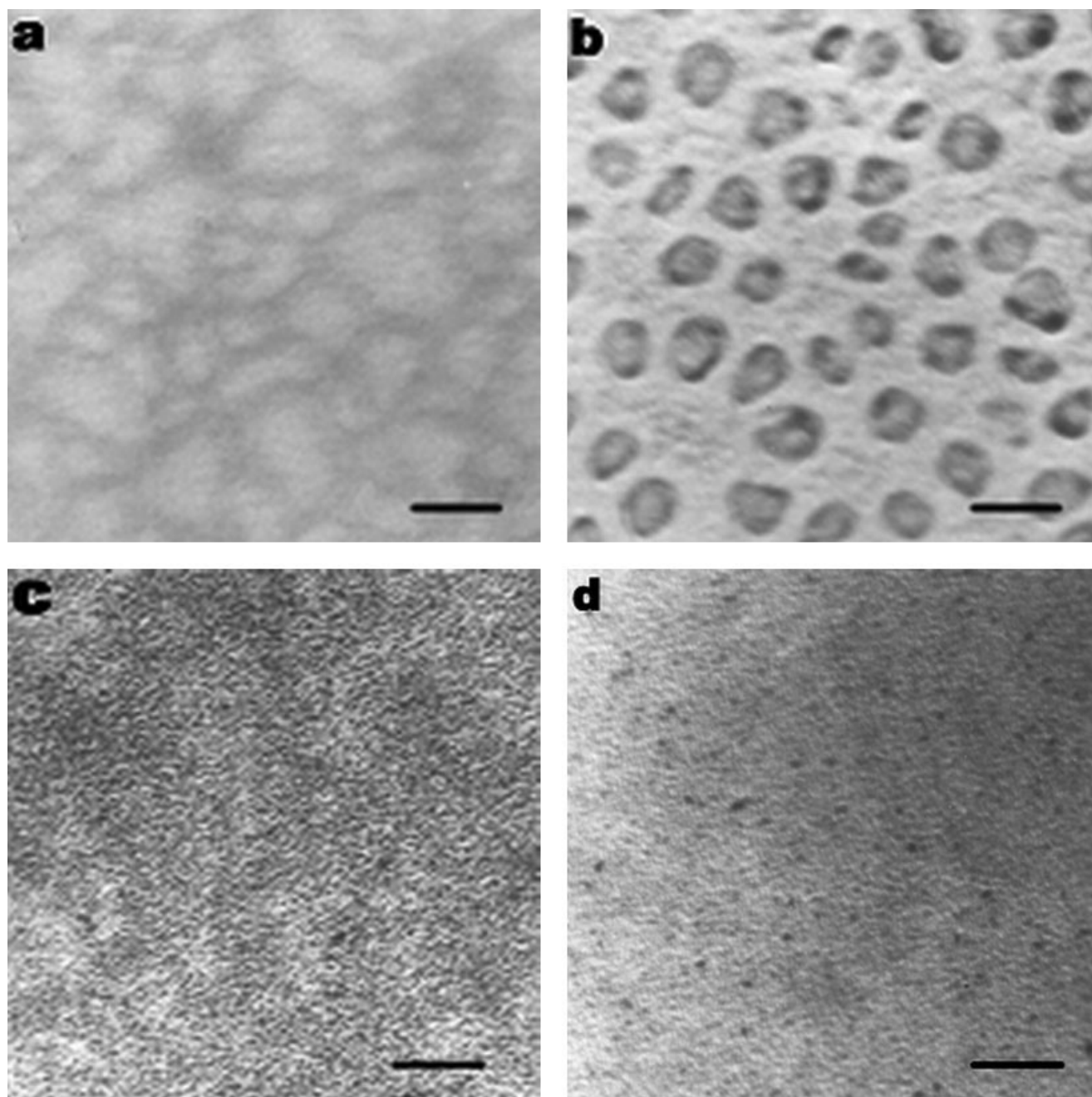


Figure 4 TEM photographs of PS-g-PEG copolymers: (a) SP28, (b) SP37, (c) SP45, and (d) SP66. Scale bars = 100 nm.

PEG island), respectively. But at high PEG content (i.e., SP45 and SP66), the films demonstrated bicontinuous PS and PEG phases, and the interdomain spacing was about 10 nm.

The surface morphologies of the PS-g-PEG copolymer coats were observed by AFM technique and are shown in Figure 5. The AFM images of coat surfaces were strongly dependent on the composition of the copolymers. Since the Sauer et al. studies²⁰ showed that the hydrophobic and hydrophilic domains could be distinguished by the AFM technique using the ultra-light-tapping mode, the dark and light regions

in AFM topographic images are regarded as the PS and PEG phases, respectively.

A very smooth surface with a roughness of ~ 1.2 nm and no obvious microphase separation was observed for sample SP28 [Fig. 5(a,b)]. However, a spindal-like or worm-like pattern was observed for sample SP45 [Fig. 5(c,d)] and an island-sea pattern for sample SP66 [Fig. 5(e,f)], indicating that microphase separation occurred at the surface for these two samples. This phenomenon was consistent with the TEM pictures, although their morphologies were different. No obvious microphase separation at the surface of

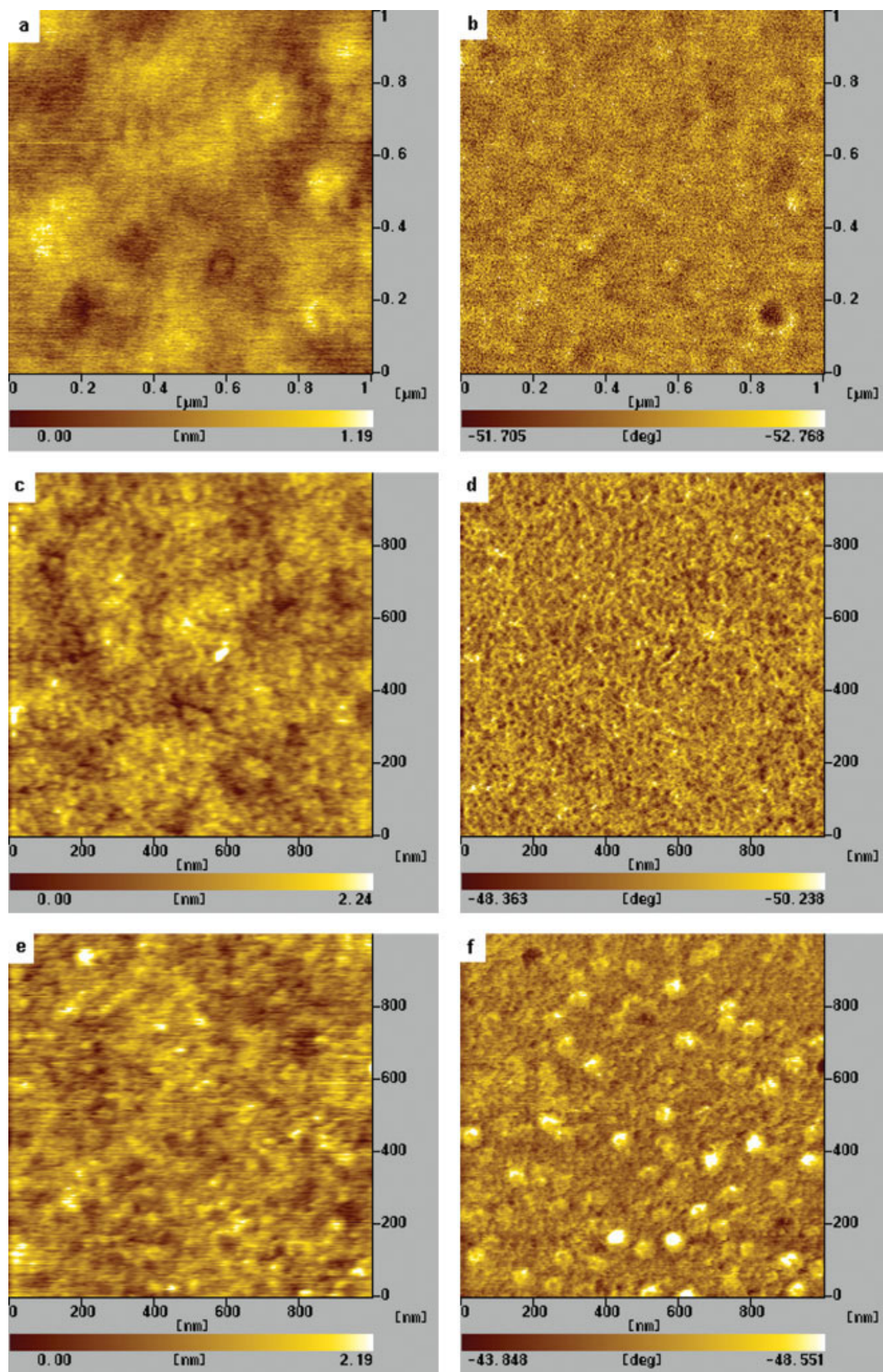


Figure 5 Topographic (a,c,e) and phase (b,d,f) images of the graft copolymers: (a,b) SP28, (c,d) SP45, (e,f) SP66. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

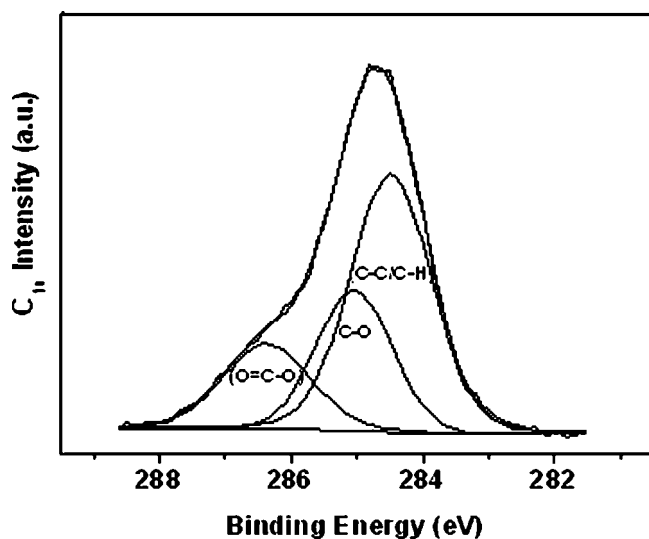


Figure 6 XPS spectrum of the C_{1s} region of a graft copolymer (SP45).

the sample with a low content of PEG (SP28) could be due to the enrichment of PS segments at the surface because of its low surface free energy. With the increment of PEG segments, PS could not fully cover the PEG domains at the surface, thus leading to the appearance of a microphase separated surface.

Surface composition of PS-g-PEG copolymer coats

The surface composition of copolymers was analyzed by XPS. A typical example of a C_{1s} XPS spectrum is provided in Figure 6. To obtain quantitative data, all C_{1s} spectra were fitted with three peaks belonging to C-C/C-H, C-O, and O=C-O according to their binding energies (as shown in Fig. 6). The peak areas were quantified using a Gaussian-Lorentzian fitting proce-

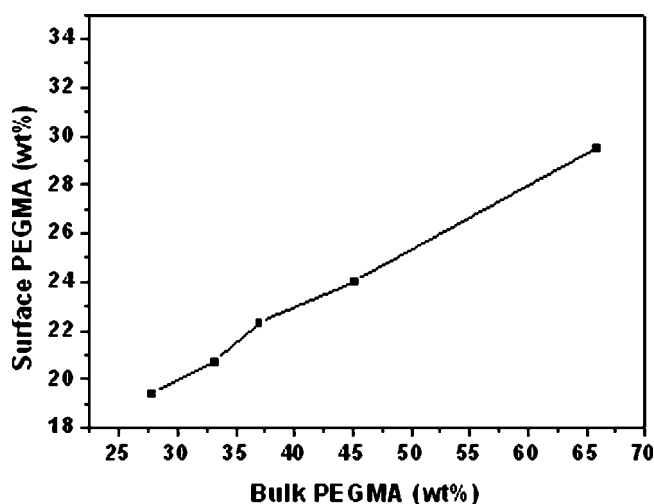


Figure 7 Surface vs. bulk composition of PS-g-PEG copolymers.

dure. These areas were interpreted as relative concentrations of the atoms involved, and then the chemical composition of the coat surface could be calculated.

The PEG concentrations at the surface of copolymer coats, determined by XPS, were compared with those in the bulk, determined by 1H -NMR, in Figure 7. It could be seen that the concentration of the PEG component at the coat surface was lower than its bulk concentration in graft copolymer, demonstrating that PS segments tended to enrich at the surface more than PEG segments. Moreover, Figure 7 also shows that the concentration of the PEG component at the coat surface increased almost linearly with its bulk concentration, which was consistent with the AFM results, namely, more PEG domains were observed at the surface for the copolymer with high PEG content.

The microphase separated structure at the surface of the PS-g-PEG copolymer coats might be formed by the following mechanism: From the thermodynamic viewpoint, PS segments were more favored to accumulate on the uppermost surface than PEG segments due to its lower surface free energy (the surface free energies of PS and PEG are 39.4 and 44.0 mN/m at 20°C, respectively²¹). On the other hand, PEG is a semicrystalline polymer and the T_g of amorphous PEG segment was below room temperature, and PEG segments were located in the side chains of the graft copolymer, while PS segments had a T_g above ambient temperature and acted as the backbone chain. This demonstrates that PEG segments had greater flexibility and mobility than PS segments under ambient conditions during coat drying. Thus, from the dynamic viewpoint, PEG segments would easily move to the copolymer-air interface at ambient conditions. Just because of the competition between thermodynamic and dynamic reasons, a microphase separated pattern occurred at the copolymer-air interface.

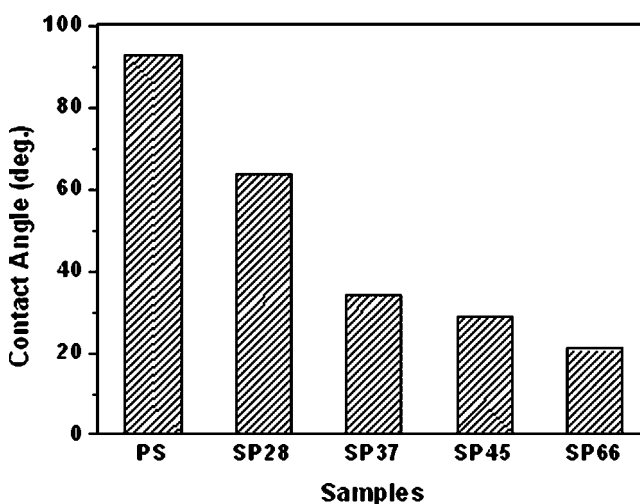


Figure 8 Static contact angle vs. bulk composition of PS-g-PEG copolymers.

Surface wettability of PS-g-PEG copolymer coats

Since PS-g-PEG was an amphiphilic polymer which has both hydrophobic PS segments and hydrophilic PEG segments, the surface wettability of the copolymer coats definitely varied with the change of its composition. The static contact angle (θ_s) of water is usually used to evaluate the surface wettability of solid polymers in air. As expected, the θ_s of water upon the coat surface gradually decreased as the weight of the hydrophilic PEG components in copolymers increased (Fig. 8). Because θ_s was only related to the outermost 10 Å of each sample, θ_s was greatly correlated with the surface composition of copolymers. Thus, the trend in Figure 8 indicates that the relative PEG content at the copolymer-air interface increased with increasing PEG weight percentage in copolymers, which was consistent with the result obtained from the XPS analysis.

In addition, the contact angles for sample SP28 changed very slowly with time during the test, while they quickly decreased for samples SP45 and SP66, which should be due to the water absorption into the PEG nanochannels, thereby indirectly indicating that some PEG segments were exposed at the outermost surface for these samples. By contrast, a polystyrene homopolymer surface displayed hydrophobic behavior, with a constant contact angle of $93 \pm 1.0^\circ$ over the duration of the experiment.

CONCLUSIONS

A PS-g-PEG copolymer was successfully synthesized by the "grafting-through" process. Both DSC analysis and TEM observation indicated that the graft copolymers had a microphase separated structure that should be caused by the incompatible PS and PEG segments. XPS and contact angle measurements also showed that there existed PEG segments at the outermost surface of the copolymer coats, although their surface free energy was larger than that of the PS segments. The existence of both PEG and PS domains at

the surface contributed to the microphase separated pattern in the coats surface. However, the microphase separated pattern was not obvious when the PEG content in the PS-g-PEG copolymer was low.

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