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Morphology of associated polymer blends: one-end-aminated polystyrene/one-end-carboxylated or sulfonated poly(ethylene glycol)

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Small-angle X-ray scattering (SAXS) profiles have been measured for blends of one-end-aminated polystyrene (APS) and one-end-carboxylated or -sulfonated poly(ethylene glycol) (CPEG or SPEG) with weight fraction of 50/50 per cent. In the profiles of blend solutions in toluene (TL), APS/CPEG/TL and APS/SPEG/TL with solvent weight fraction of 0.2 at 80°C, there exists a scattering maximum around a Bragg spacing of 203 Å for the system containing SPEG, whereas there is no peak for the system containing CPEG. Similarly, the scattering peak is absent in the profile of the blend APS/CPEG without solvent, and is observed in that of APS/SPEG at 80°C. The APS/SPEG blend sample cooled to a temperature below the melting point of SPEG shows a more intense SAXS peak than that at higher temperature. The similarly cooled blend of APS/CPEG exhibits a weak scattering maximum, and its position is nearly identical to that of pure CPEG. From these observations and previous studies on the phase diagram of blend solutions in TL, it has been suggested that the APS/SPEG blend behaves like a diblock copolymer owing to the strong association between the terminal amino and sulfonic acid groups, and an ordered structure that is similar to those observed in diblock copolymers is formed even in bulk melt and concentrated solution. Because of the weak association between amino and carboxyl groups, the APS/CPEG system behaves like an ordinary polymer blend, and crystallization of the CPEG chain may occur in a similar manner to the homopolymer in the macroscopically separated domain. Copyright © 1996 Elsevier Science Ltd.

(Keywords: functional polymer; small-angle X-ray scattering; associated blends)

INTRODUCTION

A blend system consisting of two polymers that are able to associate with each other by means of functional groups at one end of the respective polymer chains may exhibit a wide variety of phase behaviour according to the strength of the association of the end-groups and the segmental segregation strength[1–7]. At the limit of strong association, the blend behaves like a mixture of diblock copolymer and homopolymer; while at the limit of weak association, it behaves like an ordinary polymer blend.

In the previous study[1], we took a blend solution of one-end-aminated polystyrene (APS), one-end-carboxylated poly(ethylene glycol) (CPEG) and toluene (TL), and investigated the miscibility by measuring the solvent content of the cloud point at fixed temperature. As suggested by infra-red spectroscopy measurement for the blend system[4], the end-groups of these polymers associate through ionic interaction caused by proton transfer from the carboxyl group to the amino group. The cloud-point solvent concentration as a volume fraction was obtained as a function of the volume fraction of CPEG in the total polymer fraction of the blend, as indicated in *Figure 1a*. The Flory–Huggins type theory for associated polymer blend solutions could interpret the experimental results well. The association between amino and carboxyl groups was not strong enough to produce the two-peak phase diagram that was theoretically expected for a strongly associated system[6,7].

In order to realize a more strongly associated blend, we took a blend solution consisting of APS, TL and one-end-sulfonated poly(ethylene glycol) (SPEG)[2]. In the phase diagram for APS/SPEG/TL, the cloud-point curve had two peaks (*Figure 1b*) probably because of the strong association between amino and sulfonic acid groups. Actually, the association constant K_{ab} for the pair of amino and sulfonic acid groups became 700 in order to show the two-peak cloud-point curve theoretically[2], which was considerably larger than that for the pair of amino and carboxyl groups ($K_{ab} = 53$)[1]. However, the theory assuming a disordered state could not interpret the experimental results quantitatively. From these considerations, the possibility of formation of ordered structure, e.g. lamellar or cylindrical structure observed in a diblock copolymer, was pointed out in the region between the two peaks.

Morphological studies of associated polymer blends in the bulk state have been investigated by the methods of,

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for example, small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and optical microscopy. Russell *et al.*[3] reported the SAXS studies on blends of polymers having functional groups at both ends or one end. The morphologies of solvent-cast samples resembled those seen in covalently bonded block copolymers. SAXS, SEM and TEM observations of amorphous and crystalline polymer blends, consisting of polystyrene (PS) containing amino groups and poly(ethylene glycol) (PEG) containing carboxyl or sulfonic acid groups at both ends or one end, were investigated by Iwasaki *et al.*[4,5]. They presented systematic results of variation of morphologies depending on the strength of association, the nature of the casting solvent, molecular weight, fractional compositions of the segments, and so on. The well-ordered microphase-separated structure for the polymer blends of aminated PS and sulfonated PEG suggested that the associated pair of polymers behaved like a block copolymer by the formation of a complex.

In this study, we investigate morphological structures of blends of APS/CPEG and APS/SPEG in molten, solid and solution states by small-angle X-ray scattering (SAXS) measurements. The SAXS profiles have shown variety depending on the strength of association between the functional groups and temperature. The behaviour of the associated polymers and morphologies in various states has been discussed on the basis of the peak position and height of the SAXS intensity profile.

EXPERIMENTAL

One-end-aminated polystyrene (APS) was synthesized by amination of the living end of anionically polymerized polystyrene. One-end-carboxylated and -sulfonated poly(ethylene glycol)s (CPEG and SPEG) were prepared by carboxylation and sulfonation of a hydroxyl group at one end of poly(ethylene glycol). Weight-average molecular weight M_w, polydispersity index M_w/M_n and functionality of the samples are listed in *Table 1*. Toluene (TL) for solvent was used after fractional distillation.

Blend samples were prepared by dissolving two equivalent weights of polymers in benzene (about 20 mg/1 ml) and subsequently evaporating off the benzene at room temperature. The resulting blend sample was dried *in vacuo*, put into a glass capillary with the diameter of ca. 2.0 mm for X-ray scattering measurement, and gathered at the bottom of the capillary by centrifuging at a temperature of 80–100°C. For measurement of the blend solution, toluene was added to the capillary, followed by flame-sealing.

SAXS measurements were carried out by using double-mirror point-focusing optics[8]. This collimator system consisted of horizontal and vertical total-reflection mirrors, the surfaces of which are nickel-coated. The X-ray source was a rotating-anode generator (RU-200BH, Rigaku Corp., Japan) with fine focus operated at 40 kV and 100 mA. The Cu Kα line of wavelength $\lambda = 1.5418$ Å was used as the incident beam by eliminating other lines with nickel foil and two nickel-coated mirrors. A two-dimensional imaging plate (R-Axis IID, Rigaku Corp.) with an area of $200 \times 200\,\text{mm}^2$ and resolution of 0.105 mm was used as the detector. The distance from the sample to the detector was 384 mm, and the air in the path of the incident and scattered X-rays was replaced by helium gas. The glass capillary was placed in a copper heating block, the temperature of which was maintained within ±0.1 K. The two-dimensional intensity data recorded on the imaging plate by the transmission method were averaged over polar angles in the detector plane, and the scattered intensity was obtained as a function of the scattering angle 2θ. This intensity was first corrected for the self-exposure of the imaging plate[9], and normalized by the transmittance of the sample and the intensity of the incident beam. The scattered intensity

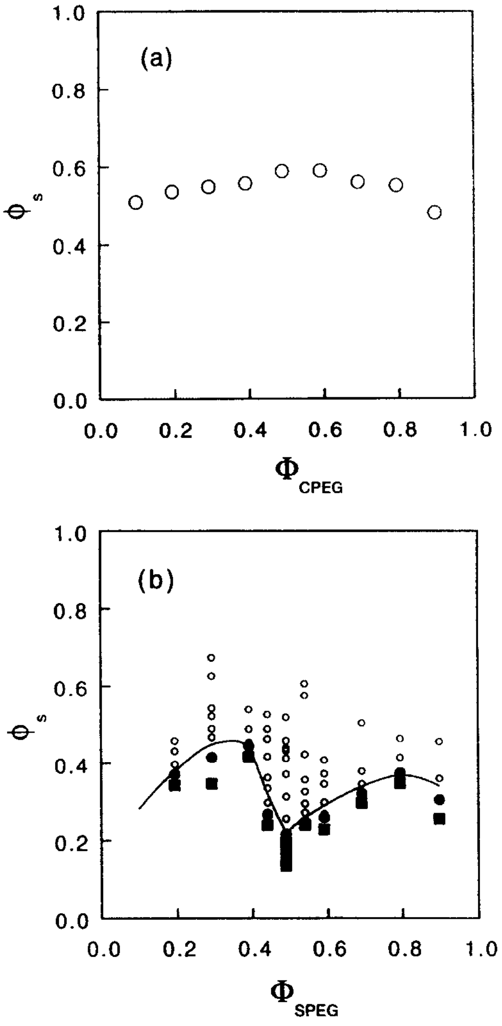

Figure 1 Quasi-binary representation of cloud-point solvent concentrations (ϕ_s) *versus* volume fraction of PEG in the total polymer fraction (Φ_{CPEG} or Φ_{SPEG}) for (a) APS/CPEG/TL at 90°C and (b) APS/SPEG/TL at 80°C. In (b): (○) clear, (●) slightly cloudy, and (■) heavily cloudy, after 2 h

Table 1 Characteristics of sample polymers

	Code	M_w^a	M_w/M_n^b	F^c
Polystyrene				
one-end aminated	APS	5600	1.06	1.00
Poly(ethylene oxide)				
one-end carboxylated	CPEG	5700	1.05	0.96
one-end sulfonated	SPEG	5700	1.05	0.99

[a] Determined by M_n with M_w/M_n, where M_n was measured by vapour-pressure osmometry
[b] Determined by size exclusion chromatography
[c] Functionalities of amino, carboxyl and sulfonic acid groups

of the sample was evaluated by subtraction of the scattered intensity of the blank capillary from those of the sample with the capillary.

RESULTS

The results of SAXS measurements for APS/CPEG and APS/SPEG systems are indicated in *Figures 2* and *3*, respectively, as the relative scattered intensity against 2θ. The profiles in *Figures 2a* and *3a* are for blend solutions, APS/CPEG/TL and APS/SPEG/TL with weight fraction of 40/40/20 per cent, at 80°C. This composition and temperature correspond to the position near the bottom between the two peaks observed in the phase diagram for the APS/SPEG/TL system[2] (see *Figure 1b*). In the profile of APS/CPEG/TL, in which the one-end amino and carboxyl groups are weakly associated with each other as suggested by the phase diagram study[1], the intensity increased monotonically with decrease of scattering angle and no intensity maximum or shoulder was observed. On the other hand, the profile for the strongly associated blend, APS/SPEG/TL, exhibited a scattering peak at $2\theta = 0.43°$, as shown in *Figure 3a*.

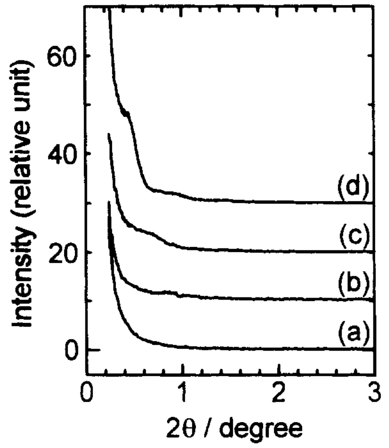

Figure 2 SAXS profiles for (a) blend solutions in toluene and (b)–(d) blends without solvent for APS/CPEG. The weight fraction for the blend solutions is 40/40/20 per cent, and for blends is 50/50 per cent. The profiles (a) and (b) were measured at 80°C, and (c) and (d) at 40°C. The samples for (c) and (d) were prepared by quenching and slow cooling, respectively, from the molten state to 0°C. The curves (b), (c) and (d) are displaced by factors of 10, 20 and 30, respectively, in order to avoid overlapping

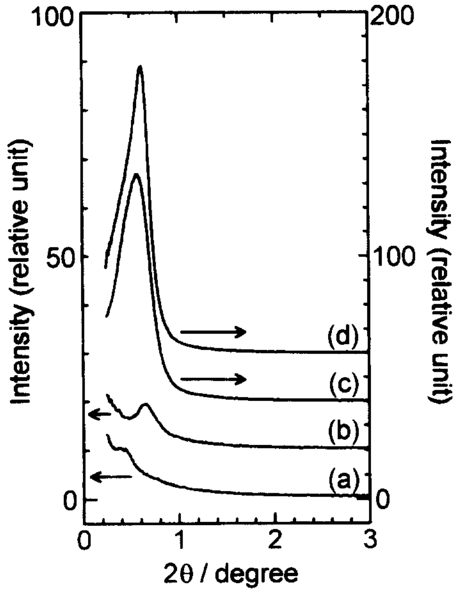

Figure 3 SAXS profiles for (a) blend solutions in toluene and (b)–(d) blends without solvent for APS/SPEG. The curves (b), (c) and (d) are displaced by factors of 10, 40 and 60, respectively. See legend to *Figure 2*

In order to investigate the characteristics of the structure formed in the blend samples, we also measured the SAXS profiles for the systems without solvent at 80°C (*Figures 2b* and *3b*). A maximum of scattered intensity could be recognized for APS/SPEG but not for APS/CPEG, which was similar to the case of the blend solutions. The scattered intensity and the value of 2θ at the maximum for the bulk APS/SPEG were larger than those of its solution.

Cooling of these melted blends to lower temperature induced crystallization of the PEG chain. The profiles in *Figures 2c* and *3c* are those for samples prepared by quenching the molten blends (80–100°C) in ice water, and samples for *Figures 2d* and *3d* were prepared by cooling them slowly from the molten state to 0°C over more than one hour. All SAXS profiles for these solidified blends were measured at 40°C. The profile in *Figure 2d*, for the slowly cooled APS/SPEG, showed the appearance of a shoulder peak at a scattering angle $2\theta = 0.48°$, which was in contrast to the profile at 80°C. The rapidly cooled APS/CPEG, *Figure 2c*, also gave a very broad shoulder around 0.6°. On the other hand, the rapidly and slowly cooled samples of APS/SPEG exhibited a considerably enhanced intense scattering maximum as shown in *Figures 3c* and *3d*. The peak for the slowly cooled APS/SPEG was asymmetric and exhibited a shoulder at lower angles, and the peak for the rapidly cooled one was rather broad. Although the first-order peak was very intense, no higher-order peaks were recognized.

Figures 4 and *5* show SAXS profiles for the pure CPEG and SPEG, respectively, which were prepared by the same thermal treatment as for the blends in order to make a comparison with those of blend samples. At 80°C, the molten CPEG and SPEG showed very weak scattered intensity as compared with the blend systems

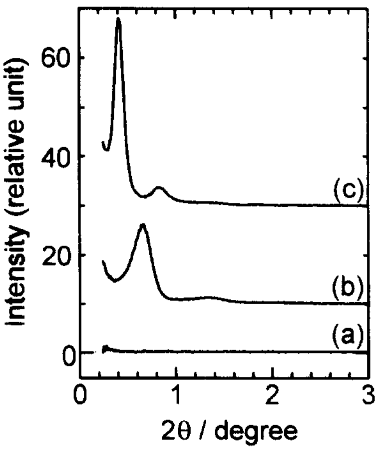

Figure 4 SAXS profiles for pure CPEG in (a) molten state at 80°C and (b)–(c) crystalline state at 40°C. The samples for (b) and (c) were prepared by quenching and slow cooling, respectively, from the molten state to 0°C. The curves (b) and (c) are displaced by factors of 10 and 30, respectively, in order to avoid overlapping

(*Figures 4a* and *5a*). After cooling to 0°C, the scattering curves showed first- and higher-order peaks, which indicates the presence of well-developed alternating crystalline and amorphous layers. The peaks in the profiles of slowly and rapidly cooled samples were sharp (*Figures 4c* and *5c*) and broad (*Figures 4b* and *5b*), respectively. Probably because of the degradation of the SPEG chain by means of the strong acidity of the sulfonic acid[2], the intensity of the peak for SPEG was weaker than that of CPEG.

For the observed first-order scattering maxima in *Figures 2–5*, the Bragg spacings $D(=\lambda/2\sin\theta)$ were calculated and are summarized in *Table 2*. The values of the spacing of the slowly and rapidly cooled samples for APS/CPEG, SPEG and CPEG were found to be similar to each other; that is, although there was no scattering maximum in the profile at 80°C, a weak peak was observed at a spacing of ca. 200 Å when the sample was slowly cooled, and at ca. 130 Å when rapidly cooled. However, these features were not recognized in the profiles for APS/SPEG. A scattering maximum could be observed distinctly even in the molten state at 80°C, and a more intense peak appeared at a spacing of about 150 Å when the sample was cooled to 0°C. These observations indicate the formation of different types of morphology in the molten and solid APS/SPEG from those of the other blend or homopolymers. The presence of the scattering maximum in the profile of the solution, APS/SPEG/TL at 80°C, also suggests the formation of a similar morphology to that observed in a bulk sample.

DISCUSSION

The scattering maximum was observed in the SAXS profile for APS/SPEG at 80°C at a Bragg spacing D of 135 Å (*Figure 3b*) but not observed for APS/CPEG in the region of $2\theta > 0.22°$ (*Figure 2b*). According to the random-phase approximation and mean-field theory[10], a disordered diblock copolymer with symmetric composition has an intensity maximum at $q_m = (4\pi/\lambda)\times\sin\theta \simeq 2/R_g$ in the scattering profile, where R_g is radius of gyration of the entire diblock copolymer. From this equation with the observed value of $q_m = (2\pi/D)$ for APS/SPEG at 80°C, the radius of gyration R_{g,q_m} was obtained as 43.0 Å. This value can be compared with the unperturbed dimension $R_{g,0} = 31.4$ Å, which was calculated by using the characteristic ratio of dimensions $\langle r^2\rangle/nl^2$ of PS and PEG chains in the unperturbed state[11] and the relation $R^2_{g,0} = R^2_{g,PS} + R^2_{g,PEG}$. The similarity in the order of magnitude between R_{g,q_m} and $R_{g,0}$ indicates the formation of a diblock-copolymer-like structure due to the strong association between the terminal $-NH_2$ and $-SO_3H$. Moreover, the fact that R_{g,q_m} is larger than $R_{g,0}$ may suggest the deviation from Gaussian behaviour in the disordered state near the order–disorder transition[12,13], or the formation of a microphase-separated structure in which each block chain of copolymer takes a stretched conformation perpendicular to the interface between APS and SPEG. Taking account of the similarity of the molecular weight, a lamellar structure is the most plausible for the ordered structure. The molecular-weight dependence of the lamellar domain spacing for molten diblock copolymer has been presented both theoretically[14,15] and experimentally[16]. According to Helfand *et al.*[14], the domain spacing D of a symmetric diblock copolymer with high degree of polymerization in the strong segregation limit is given by:

$$D = 1.34\chi^{1/7}bN^{9/14}$$

where χ is the Flory–Huggins interaction parameter, b is the segment length and N is the number of chain segments. Semenov[15] also evaluated the value of D as:

$$D = 1.10\chi^{1/6}bN^{2/3}$$

From the phase-diagram studies presented in the previous reports[1,2], the value of χ for PS and PEG was estimated as 0.112–0.2 per site of the volume of a toluene molecule, and the polymeric indices N obtained as the ratio of molar volume of polymer to toluene were 47 and 46 for APS and SPEG, respectively. Using these values of N and the unperturbed dimensions of PS and PEG[11], the values of b were evaluated as 7.4 Å for APS and 8.5 Å for SPEG; thus $b = 7.9$ Å was adopted as the average value. With these parameters, the lamellar domain spacings were calculated as 144–156 Å and 125–137 Å by the theories of Helfand *et al.*[14] and Semenov[15], respectively. These values revealed good agreement with the experimentally obtained one (135 Å), which suggests the formation of ordered lamellar structure in the APS/SPEG system at 80°C. With these considerations, we depicted a conceivable structure for molten APS/SPEG in *Figure 6a*. The strongly associated polymers between $-NH_2$ and $-SO_3H$ behave as a covalently bonded diblock copolymer and form the ordered lamellar structure. On the other hand, the pair of APS and CPEG in which amino and carboxyl groups are weakly associated with each other behaves not like a diblock copolymer but like an ordinary polymer blend. In the latter case, a macrophase separation as illustrated in *Figure 6c* would

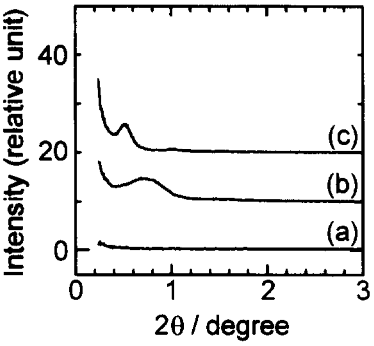

Figure 5 SAXS profiles for pure SPEG. The curves (b) and (c) are displaced by factors of 10 and 20, respectively. See legend to *Figure 4*

Table 2 Bragg spacings (Å) of the first-order peaks

Sample	80°C	40°C after slow cooling	40°C after rapid cooling
APS/CPEG/TL	*a*	–	–
APS/SPEG/TL	203	–	–
APS/CPEG	*a*	184	138
APS/SPEG	135	142	152
CPEG	*a*	215	134
SPEG	*a*	172	124

[a] Not observed

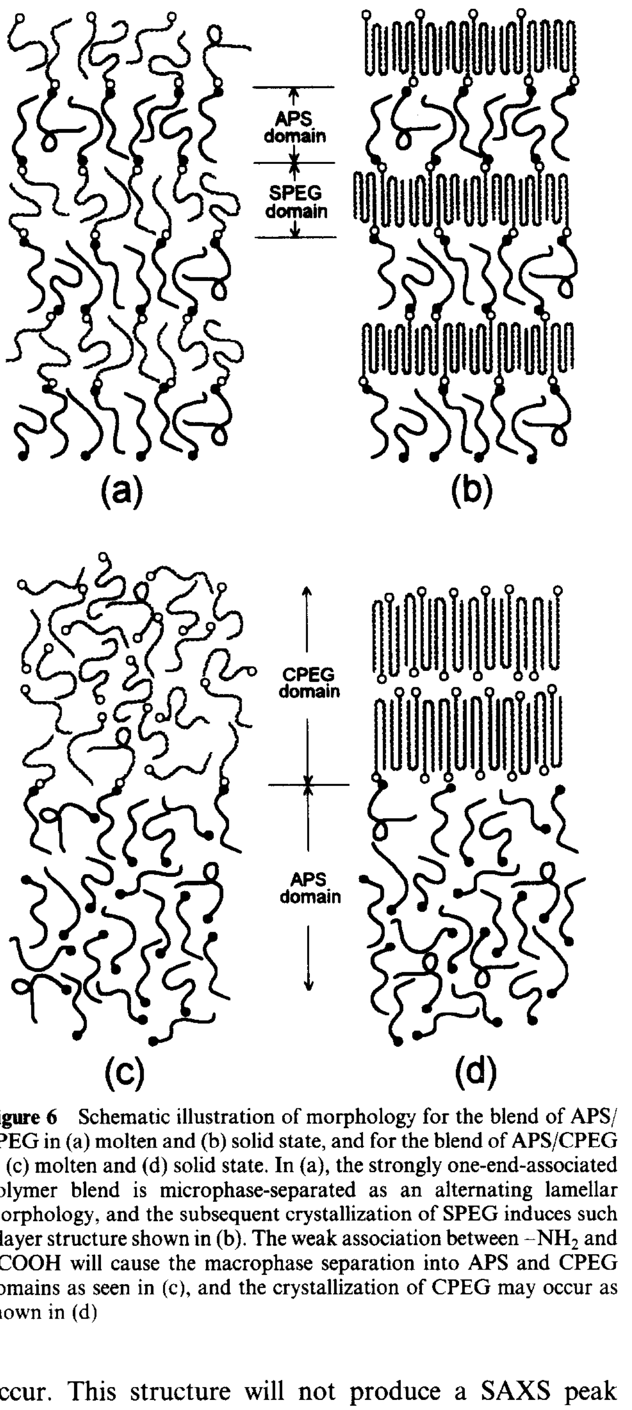

Figure 6 Schematic illustration of morphology for the blend of APS/SPEG in (a) molten and (b) solid state, and for the blend of APS/CPEG in (c) molten and (d) solid state. In (a), the strongly one-end-associated polymer blend is microphase-separated as an alternating lamellar morphology, and the subsequent crystallization of SPEG induces such a layer structure shown in (b). The weak association between $-NH_2$ and $-COOH$ will cause the macrophase separation into APS and CPEG domains as seen in (c), and the crystallization of CPEG may occur as shown in (d)

occur. This structure will not produce a SAXS peak within the measurable range of scattering angle.

After cooling the blend of APS/SPEG from 80°C to 0°C, the intensity of the scattering peak was enhanced without changing its position (*Figures 3c* and *3d*, and *Table 2*). From this observation and the structure at 80°C (*Figure 6a*), the possible structure in the solid state is indicated in *Figure 6b*. First, the microphase-separated structure at higher temperature would freeze in the cooling process by glass transition of the PS domain. Since subsequent crystallization of the PEG chain must take place in the confined space between the PS layers, the change of the lamellar domain spacing during cooling becomes small. Moreover, the crystallization of the PEG chain causes the enhancement of electron-density difference between the neighbouring layers in the lamellar structure (electron density at 40°C is $339\,e\,nm^{-3}$ for PS, $366\,e\,nm^{-3}$ for amorphous PEG, and $403\,e\,nm^{-3}$ for crystalline PEG), which makes the SAXS peak more

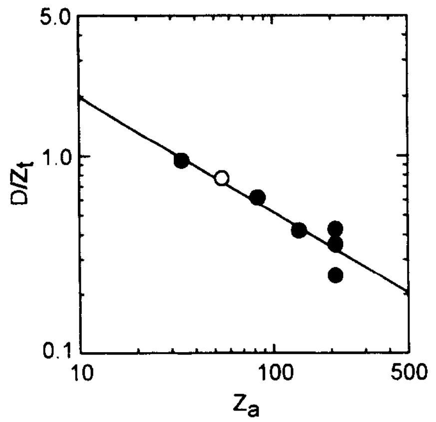

Figure 7 Double-logarithmic plot of the reduced lamellar domain spacing, D/Z_t, against the degree of polymerization of amorphous block, Z_a. Filled circles: PS-*block*-PEG cited from refs. 17 and 18. Open circle: APS/SPEG blend (in this case, the total degree of polymerization, Z_t, is taken as the sum of those of APS and SPEG). The best-fit straight line for the filled circles is also indicated

intense. On the other hand, the blend of APS/CPEG showed a weak SAXS maximum, the scattering angle of which was similar to that for pure CPEG at lower temperature (*Figures 2c* and *2d*, and *Table 2*). It may be considered that the macrophase-separated CPEG chain would crystallize independently of the state of the APS domain as illustrated in *Figure 6d*, and the ordinary alternating crystalline–amorphous layer structure like a crystalline homopolymer will be formed in the CPEG domain.

The results for APS/SPEG may be compared with the diblock copolymers comprising crystallizable and amorphous segments. Structural studies of diblock copolymers, PS-*block*-PEG, were investigated by means of SAXS measurement by Gervais *et al.*[17,18], and the equilibrium theory for microphase separation on the amorphous–crystalline diblock copolymer has been presented by Whitmore *et al.*[19]. According to the theoretical result, the lamellar domain spacing for an amorphous–crystalline diblock copolymer is expressed as:

$$D \sim Z_t Z_a^{-5/12}$$

where Z_t is the total degree of polymerization and Z_a is the degree of polymerization of the amorphous block. Experimental verification for this equation was investigated by Douzinas *et al.*[20], i.e. the best-fit line for the plot of $\ln(D/Z_t)$ *versus* $\ln(Z_a)$ for diblock copolymers of (ethylene-*co*-butylene)-ethylethylene had the slope of -0.42, which was nearly identical with $-5/12$. The lamellar domain spacing obtained for the diblock copolymers PS-*block*-PEG, cited from refs. 17 and 18, are plotted as $\ln(D/Z_t)$ *versus* $\ln(Z_a)$ by filled circles in *Figure 7*. According to Gervais *et al.*[17,18] all the samples prepared by rapid cooling of the melt (90°C) formed a lamellar structure; thus their results can reasonably be compared with ours for the associated blend APS/SPEG. The best-fit line drawn in the figure has the slope of -0.58, smaller than $-5/12$, probably because the equilibrium morphology was not achieved. The result for APS/SPEG obtained in this work is also plotted in *Figure 7* by the open circle, which is adequately predicted by the fitted line for the diblock copolymers. Thus, it seems reasonable to say that the pair of APS and

SPEG behaves as a diblock copolymer due to the strong association between $-NH_2$ and $-SO_3H$ in the solid state as shown in *Figure 6b*. Gervais *et al.*[17,18] also reported the morphology for molten PS-*block*-PEG. Because of the similarity of the molecular weights, their results for the copolymers SEO4 (PS–PEG diblock copolymer with $M_{n,PS} = 3500$ and $M_{n,PEG} = 5500$) and SEO5 ($M_{n,PS} = 8800$ and $M_{n,PEG} = 5500$) are comparable with our blend system. However, the molten SEO5 was suggested to form a hexagonal mesophase structure, and it was not clear whether SEO4 formed a mesophase or not. On the other hand, the higher-molecular-weight polymer SEO8 ($M_{n,PS} = 22\,100$ and $M_{n,PEG} = 20\,400$) had symmetric composition and was shown to give a lamellar domain spacing of ca. 250 Å when the PEG chain was melted, and ca. 240 Å when the PEG chain was crystallized. This result suggests that the method of melt-quenching from microphase-separated state to crystallizable temperature for an amorphous–crystalline diblock copolymer does not produce a considerable variation in the periodic spacing of lamellae. The structure depicted in *Figures 6a* and *6b* for APS/SPEG seems consistent with these observations for the PS-*block*-PEG[17,18].

Iwasaki *et al.*[4,5] studied the morphology of a blend of terminal aminated PS and carboxylated or sulfonated PEG prepared by solvent casting using various solvents. The pair of one-end-aminated PS and sulfonated PEG formed an ordered lamellar structure, which was confirmed by TEM observation and a sharp scattering maximum in the SAXS profile. The reported value of the Bragg spacing D obtained from the SAXS profile for the blend of APS ($M_w = 6400$) with SPEG ($M_w = 6000$) was 217 Å at room temperature. This is somewhat larger than our results (142–152 Å at 40°C and 135 Å at 80°C) even though the molecular weights are larger than ours, and larger than the predicted value (136 Å) by the best-fit line for the PS-*block*-PEG in *Figure 7*. As commented by Iwasaki *et al.*[4], it might be considered that the crystallization of PEG chain occurred before microdomain formation during the solvent casting. We adopted the melt-quenching method, in which the crystallization of the PEG chain may occur after microphase separation and the growth of the crystalline domain is hindered by the PS domain as shown in *Figure 6b*. These differences in the process of the formation of the ordered structure will cause dissimilar periodic spacing of the lamellar structure.

The blends of one-end-aminated PS and carboxylated PEG were reported to show a more disordered periodic structure[4], which was in contrast to the case of the sulfonated PEG[5]. This observation is comparable with our results of the phase diagrams[1,2] and SAXS measurements in solution and molten state. As discussed above, the strong association between APS and SPEG induces the formation of diblock-copolymer-like structure and microphase-separated lamellae as depicted in *Figure 6*. The formation of ordered structure was also observed even in the APS/SPEG/TL system with the weight per cent of 40/40/20. As has been pointed out in the previous study[2], the cloud-point curve for APS/SPEG/TL had two peaks (*Figure 1*), probably because of the strong association between the terminal amino and sulfonic acid groups, and it was hard to interpret the experimental result quantitatively by the mean-field theory for disordered mixtures. The present SAXS measurements suggest the necessity to consider the presence of the ordered phase in the region between the two peaks. The quantitative disagreement between experimental and theoretical results for the strongly associated polymer blend should be caused by the formation of the ordered structure that was not taken into account in the Flory–Huggins type theory for the associated polymer blends presented in the previous paper[1,2].

CONCLUSION

The morphologies of associated polymer blends, i.e. APS with CPEG and APS with SPEG, have been investigated by SAXS measurement. In the case of strong association between $-NH_2$ and $-SO_3H$ sufficient to produce two peaks in the phase diagram of APS/SPEG/TL, the pair of associated polymers behaves like a diblock copolymer and forms a microphase-separated structure at 80°C as revealed by the presence of a SAXS peak. On the other hand, weak association between $-NH_2$ and $-COOH$ induces macrophase separation into PS and PEG domains at high temperature. Crystallization of the PEG chain by subsequent cooling may be considered to occur in the preserved microphase- and macrophase-separated domains. These structural models indicated in *Figure 6* can explain the temperature variation of the SAXS profiles.

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