Morphology of Blends of α,ω-Diaminopolystyrene with α,ω-Dicarboxypoly(ethylene oxide)

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ABSTRACT: The morphology of blends of polystyrene (APS) with poly(ethylene oxide) (CPEO) having amino and carboxy groups at the respective chain ends was investigated by small-angle X-ray scattering (SAXS), transmission electron microscope (TEM), and scanning transmission microscope (SEM) measurements. SAXS measurement of films of equimolar APS/CPEO blends cast from preferential solvents for APS or good solvents for both telechelics showed the formation of a periodic structure where the period increased with the molecular weight of APS. Lamellar structures were observed by TEM in the cross section of the blend films and the period of the lamellar layer fairly agreed with those measured by SAXS. The layer structure was also clearly observed by SEM everywhere in the cross section of the fractured film, indicating that the interaction of the chain ends between APS and CPEO induced regular structure. Surface analysis of the blend by X-ray photoelectron spectroscopy also supported formation of the ordered structure near the surface. On the other hand, the APS/CPEO blend film cast from a nitromethane/THF mixture, a preferential solvent for poly(ethylene oxide), included significantly disordered structure. FT-IR spectra of the APS/CPEO blend showed that partial proton transfer occurred from the carboxy group of CPEO to the amino group of APS. After washing of the polymer blend film in cyclohexane at 40 °C, the molar ratio of APS/CPEO in the insoluble part was measured by ^{1}H NMR, indicating that 35–70% of APS was bound to CPEO.

Introduction

Polymers which have complementary binding sites on each repeating unit, such as acid–base, proton donor–acceptor (hydrogen bonding), electron donor–acceptor, and ligand–metal salt, associate with each other to form the stoichiometric "intermacromolecular complex".[1] The complexes generate three-dimensional networks through strong interaction between the binding sites, occasionally resulting in precipitation and gelation. Recently, sporadic introduction of the interacting groups to polymer chains has been studied to enhance compatibility of the otherwise immiscible polymer pair by many researchers.

Eisenberg and his co-workers[2-4] investigated the miscibility of several polymer blends including acid and base moieties. Polyisoprene and polystyrene bearing equivalent amounts of sulfonic acid and 4-vinylpyridine units, respectively, were found to be compatibilized at a degree of substitution as little as 5% by measurements of T_g and optical transparency. Gelation occurred in this miscible system whereas the polymer blend with a 2–3% degree of substitution was still soluble in THF and showed two T_g's. Percec et al.[5] reported the partial modification of poly(2,6-dimethyl-1,4-phenylene oxide) and poly(epichlorohydrin) by respective introduction of carbazoyl (donor) and 3,5-dinitrobenzoyl (acceptor) pendant groups. A blend of these polymers showed a single T_g with at least 25% substitution without gel formation, indicating that the electron donor–acceptor interaction also led the compatibilization of the otherwise immiscible polymer pair. A polymer miscibility study based on the hydrogen-bonding interaction was reported by Fréchet et al.[6] using copolymers of styrene with 4-hydroxystyrene (proton donor) and poly(4-vinylpyridine) (proton acceptor). By T_g measurement, poly(4-vinylpyridine) was found to be miscible over the entire range of composition, with the random copolymer containing styrene and 4-hydroxystyrene units in a 1:1 molar ratio. The equimolar complex was precipitated from methanol. Although the polymers used in these studies are partly functionalized, the stoichiometric complexation occurs in some cases of strong interaction and with a high degree of substitution of complementary binding groups, as was typically observed between fully functionalized polymer pairs. In the compatibilized blend of random copolymers, segment chains of each polymer and complexed sites are well mixed to lead to a completely homogeneous phase with a single T_g.

In contrast to the blends of random copolymers, those including telechelic polymers were found to form microheterogeneous structures having respective T_g's.[7-10] A combination of telechelic polymer and random copolymer might induce graft polymer like structure through end to pendant interaction, resulting in regular structure. Garton et al.[7] prepared "grafted copolymer networks" through the transition metal coordination between the polybutadiene terminated with copper carboxylate groups at chain ends and the polystyrene randomly containing 4.2 mol % of 4-vinylpyridine units. The coordination interaction and microphase separation were investigated by FT-IR and SAXS measurements, respectively. Combination of two telechelic polymers might also lead the block copolymer like structure. Teyssié et al.[8,9] investigated ionic interaction between telechelic polystyrene and polybutadiene end capped with amino and carboxy groups, respectively. The ionic cross-interactions of the polymer end groups resulted in a "multiblock copolymer", which was confirmed by IR and DSC measurements. Russell et al.[10] reported that microphase-separated structure was promoted by coulombic interaction between the chain end groups in the similar systems. However, the morphologies of the microphase-separated structures in those blend systems have not been directly observed yet by means of an electron microscope.

We report here the morphological study of the polymer blend between polystyrene and poly(ethylene oxide) (PEO) containing amino and carboxy groups at both chain ends, using TEM, SEM, and SAXS. PEO is a well-known crystalline polymer, whereas polystyrene anionically polymerized is amorphous. The block copolymer having crystallizable and amorphous segments has been presented to induce various types of morphology depending not only on the fractional compositions of the segments but also on the relative rate of crystallization in the ordering

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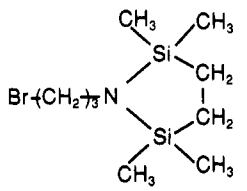
process.[11] Accordingly, the ionic interaction of end groups of the telechelic polymers, separation of each microdomain, and crystallization of PEO may proceed competitively to produce interesting ordered structures in this blend system.

Experimental Section

Preparation of Telechelic Polymers. α,ω-Diaminopolystyrenes (APS-2–15) were synthesized by an anionic living polymerization technique reported previously.[12] Styrene was distilled over calcium hydride under a nitrogen atmosphere and then over phenylmagnesium chloride on a vacuum line. The aminating reagent, 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane (1), was prepared by the reaction of 1,1,4,4-



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tetramethyl-1,4-dichloro-1,4-disilabutane with 3-bromopropylamine hydrobromide in the presence of triethylamine in dry dichloromethane. The crude product was purified by repeating fractional distillations and then distilled over phenylmagnesium chloride on a vacuum line. THF was refluxed over sodium wire for 5 h, distilled over $LiAlH_4$, and further distilled from the sodium naphthalenide solution. Pentane was washed with concentrated H_2SO_4, aqueous 1 M NaOH, and water successively and dried over $CaCl_2$. It was refluxed over CaH_2 for 10 h and distilled from the butyllithium solution. Polymerization and amination reactions were carried out under high-vacuum conditions in sealed glass reactors with break seals. Aninoic polymerization of styrene initiated with potassium naphthalenide was carried out in THF or THF/pentane 1/1 (v/v) mixed solvent at −78 °C for 0.5 h. An excess (1.5–2.0 equiv to initiator) of 1 in THF (0.2–0.4 M) was added to the THF (or THF/pentane) solution of living polystyrene at −78 °C. The resulting mixture was allowed to stand at −78 °C for 12 h and at room temperature for 1 h to complete the amination reaction. The polymer obtained was precipitated by adding the solution to a large excess of methanol and was purified by repeating reprecipitation with a benzene/methanol system at least three times followed by freeze-drying from benzene. During reprecipitation steps, the silyl protecting group was completely removed, resulting in amino functions at both ends of the polymer chain, which was confirmed by the ^1H NMR spectrum of the polymer produced. For accurate evaluation of the amino functionality, the number averaged molecular weight (M_n) of the polymer should be exactly determined. Accordingly, the M_n and the polydispersity (M_w/M_n) were estimated by size-exclusion chromatography (SEC) using standardized polystyrenes after the amino end group was benzoylated to avoid adsorption of the polymer on the SEC column. Thus, molecular weights of the telechelics were found to be exactly controlled by the monomer to initiator ratio and the values of M_w/M_n were around 1.1, as shown in Table I. The amount of amino group at the polymer chain end was determined by acid–base titration. A benzene solution of the polymer sample was titrated with standard 0.002 M $HClO_4$ in glacial acetic acid by using crystal violet as an indicator. The functionality for each polymer was estimated to be 1.8–2.0. These values of the functionality were also confirmed by the TLC/flame ionization detection technique, as was previously described.[12]

APS-1, a low molecular weight amine, was prepared as follows: THF solution of 1,1-diphenylethylene was added to a heptane solution of *n*-butyllithium under high-vacuum conditions and kept at room temperature for 10 min. After being cooled at −78 °C, a THF solution of the aminating reagent 1 was added to the resulting solution, which was kept at −78 °C for 3 h and at room temperature for 1 h. The product was treated with methanol to remove the protective group and was isolated by column chromatography on silica gel. PS-16 is a homopolystyrene without an amino group for the control experiment.

Table I
Synthesis of α,ω-Diaminopolystyrene

code	M_n(calcd)[a]	M_n(obsd)[b]	M_w/M_n	F[c]
APS-1[d]	295	295		1.00
APS-2	2100	3600	1.05	2.08
APS-3	3600	4200	1.04	2.10
APS-4	6100	5200	1.08	1.94
APS-5	4700	5800	1.11	2.16
APS-6	5700	5800	1.05	1.92
APS-7	6000	6000	1.04	1.88
APS-8	7200	6100	1.06	1.84
APS-9	9100	8900	1.03	1.90
APS-10	14000	12000	1.03	1.86
APS-11	16000	19000	1.20	1.98
APS-12	20000	22000	1.12	1.90
APS-13	26000	28000	1.02	2.06
APS-14	23000	30000	1.14	1.86
APS-15	62000	76000	1.13	1.88
PS-16[e]	11000	11000	1.05	

[a] Based on monomer to initiator ratio. [b] Measured by GPC with polystyrene calibration. [c] Amino group functionality. [d] 1-Amino-4,4-diphenylnonane. [e] Polystyrene without amino group.

α,ω-Dicarboxypoly(ethylene oxide) (CPEO) was a generous gift from Kawaken Fine Chemicals Co., Ltd., Saitama, Japan. CPEO was purified as follows: It was dissolved in aqueous 0.01 N HCl, and the solution was extracted with chloroform and evaporated to dryness. It was again dissolved in distilled water, and the resulting solution was extracted with chloroform and evaporated to dryness. The resulting polymer was purified further by reprecipitations using a benzene/hexane system at least two times. The product was freeze-dried under vacuum from benzene for 1 day. The molecular weight of CPEO was determined by SEC (M_n = 8600, M_w/M_n = 1.09) using standardized PEOs after methyl esterification of the carboxy end groups. The functionality of CPEO was estimated by acid–base titration with KOH/water (F = 2.02).

Preparation of Polymer Blend Specimen. Polymer blends were typically prepared from benzene solution. Equimolar quantities of APS and CPEO (total amount, 100 mg) were dissolved in benzene (1.5 mL) with stirring for 2 h. A film of the polymer blend was cast on a Teflon sheet (0.17 mL/cm^2) by evaporating benzene at 10–15 °C under a nitrogen atmosphere overnight. The resulting film was dried in vacuo at room temperature for 1 day. As casting solvents, chloroform, THF, ethylbenzene, 1,4-dioxane, and nitromethane/THF (5/1, v/v) were also employed.

Fourier Transform Infrared Spectroscopy (FT-IR) Measurement. FT-IR measurements of APS-1, α,ω-dicarboxypoly(ethylene oxide) (M_n = 1000, F = 1.94), and their 1:1 blend were carried out on a JEOL JIR-AQS 20M FT-IR spectrophotometer. APS-1 and α,ω-dicarboxypoly(ethylene oxide) (M_n = 1000) were directly coated onto a KBr window, and the blend was cast from benzene into a thin film on a KBr window for the IR measurement.

SAXS and WAXS Measurement. Small-angle X-ray scattering data were collected on a diffractometer (Rigaku Denki Co., Ltd.) with a position-sensitive proportional counter situated 400 mm from the samples. Wide-angle X-ray scattering measurement was performed with a proportional counter situated 200 mm from the samples. Ni-filtered Cu Kα radiation operating at 40 kV and 30 mA was used. Specimens were mounted into a sample holder with a hole of 3-mm diameter which was then sealed with a poly(ethylene terephthalate) film as the window. The degree of crystallinity of CPEO was estimated by WAXS as well as by DSC.

TEM and SEM Observation. An ultrathin section of the polymer blend for TEM observation was made as follows: The polymer blend film was dipped in 1 wt % aqueous ruthenium tetraoxide (RuO_4) solution as fixing and staining reagent for 20 min. After being dried, the film was embedded in epoxy resin and cut into ultrathin sections (700–1000 Å thick) by an ultramicrotome with a diamond knife. The sectioned specimens

were further stained with the vapor of RuO_4 for 5 min. The morphology of the section was observed by a Hitachi H-500 transmission electron microscope with 100 kV of accelerating voltage. A sample for SEM was prepared by exposing the polymer blend film to the vapor of RuO_4 as a fixing reagent for 2 h at 40 °C. The film was fractured in liquid nitrogen to get a fresh cross section just prior to observation. The morphology of the fresh section coated with Pt about 20 Å thick was examined by a Hitachi S-900 scanning electron microscope with 3 kV of accelerating voltage.

DSC Measurement. The degree of crystallinity of CPEO in the polymer blend was measured by differential scanning calorimetry (DSC), using a Perkin-Elmer DSC-2. The heat of fusion of the films cast from benzene was measured at the first heating. The degree of crystallinity of CPEO in percent was evaluated by $[\Delta H_f \times 100]/\Delta H_f^*$ where ΔH_f is the heat of fusion per mole of repeating unit of CPEO and ΔH_f^* is the heat of fusion per mole of repeating unit of perfectly crystallized PEO, 8.66 kJ/mol.[13]

X-ray Photoelectron Spectroscopy (XPS). 1. Sample Preparation. Equimolar quantities of APS (APS-6 and 10) and CPEO were dissolved in benzene (2 w/v %) and stirred for 2 h. For a control experiment, polystyrene (M_n = 5100) was also blended with CPEO in benzene. After filtration, 40 μL of the solutions was cast onto clean glass disks of 9-mm diameter under a clean hood and gradually evaporated at room temperature overnight.

2. XPS Measurement. All XPS data were collected with a Surface Science Instruments (SSI) X-Probe ESCA spectrometer using an Al Kα monochromatized X-ray source. Angular-dependent experiments were carried out at five different angles. This instrument permits analysis of the outermost ~100 Å of an elliptical area whose short axis can be adjusted from 150 to 1000 μm. All data were processed by using the standard software provided with this instrument. An electron flood gun set at 5 eV was used to minimize surface charging of the samples. The binding energy scale was referenced by setting the *C*–C, *C*–H peak maximum in the C_{1s} spectrum to 285.0 eV.

Results and Discussion

Formation of the Complex of APS and CPEO. Fréchet et al. reported that a 1:1 complex of poly(4-vinylpyridine) and poly(4-hydroxystyrene) was isolated as precipitant in methanol.[6] Although a hydrogen bonding between pyridine and phenol pendants is not a strong interaction, a large number of hydrogen bondings between polymer chains leads to an insoluble complex. Both strength and number of the complementary interaction may reflect the stability of the complex.

To isolate an insoluble aggregate of APS and CPEO, many solvent systems were examined in this study. However, the stoichiometric complex of APS and the CPEO has not been isolated yet. Only one linkage between amino and carboxy groups at the terminals of APS and CPEO may not bind the polymer chains tightly. Thus, the amount of the APS bound to CPEO was estimated by the following procedure. APS and CPEO were blended at various molar ratios in benzene and cast into a film (ca. 100 mg), which was washed with cyclohexane (5 mL) at 40 °C with stirring overnight to remove excess APS. The solvent was decanted, and the residual polymer was washed three more times with cyclohexane (5 mL) at 40 °C for 2 h. The soluble part in cyclohexane, which was evaporated to dryness, and the insoluble part were separately freeze-dried from benzene. The molar ratio of APS and CPEO in each part was determined by ^1H NMR. Since CPEO is insoluble but APS is poorly soluble in cyclohexane at 40 °C individually, the APS in the insoluble part is considered to be bound to CPEO. The soluble part is found to contain exclusively APS, which does not interact with CPEO.

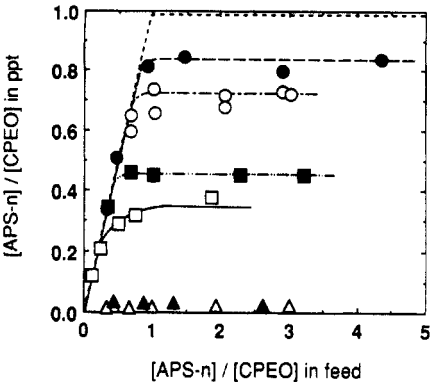

Figure 1. Formation of the complex between APS-*n* and CPEO in cyclohexane: (–●–) APS-1/CPEO blend; (– ·○· –) APS-7/CPEO blend; (– ··■··–) APS-9/CPEO blend; (–□–) APS-12/CPEO blend; (▲) PS-16/CPEO blend; (△) APS-6/PEG blend.

Figure 1 shows the relationship between the molar ratio of the telechelic polymers insoluble in cyclohexane and that in the feed. In addition, two control experiments were carried out using the polymer pairs without ionic interacting groups, i.e., homopolystyrene (PS-16)/CPEO and APS-6/poly(ethylene glycol) (M_n = 12 000) having hydroxy groups in place of carboxy groups at the chain ends. In both cases, homopolystyrene and APS-6 were mostly extracted with cyclohexane and a very small amount of polystyrenes remained in the insoluble parts, indicating that no complexation occurred in these cases. When the blend of APS and CPEO having complementary interacting groups was washed with cyclohexane, appreciable amounts of APS remained in the insoluble part against repeated extraction with cyclohexane. Especially at low feed ratios of APS to CPEO, most of the APS was found in the insoluble part, as shown in Figure 1. If a perfect 1:1 stoichiometric complex is formed, the ratio of the telechelic polymers insoluble in cyclohexane against the feeding ratio should be on the dotted line. However, the results were deviated from the stoichiometric line and leveled off at higher feed ratio. The value of the plateau decreases with an increase in the M_n of APS. Steric hindrance of the APS polymer chain would interfere with the quantitative acid–base interaction between the polymer chain ends. The plateau level was unchanged even when the extraction of cyclohexane was repeated eight times, suggesting that no dissociation of the complexation occurred under this condition. Although a 1:1 stoichiometric complex was not isolated, these results show that the interaction between amino and carboxy groups at the chain ends essentially contributes to complexation between APS and CPEO.

FT-IR Measurement. The interaction between carboxy and amino groups in the polymer blend was examined by infrared spectroscopy. Here, the relatively low molecular weight samples, α,ω-dicarboxypoly(ethylene oxide) (MW = 1000), APS-1, and their blend, were employed to obtain clear absorption bands due to the terminal groups of the polymer chains. For each telechelic polymer, stretching bands of O—H (3420 cm^{-1}), >C=O (1744 cm^{-1}), and N—H (3370 and 3265 cm^{-1}) and a deformation band of N—H (1688 cm^{-1}) were observed. On the other hand, these absorption bands were weakened and some new bands due to ammonium carboxylate appeared in the IR spectrum of the blend of PEO acid and APS-1. The stretching vibration of NH_3^+ (3188 cm^{-1}), combination vibration (2120 cm^{-1}), symmetrical and antisymmetrical N^+—H deformation vibration (1600–1500 cm^{-1} overlapping with the absorption band of C=O), and NH_3^+ torsional vibration (506 cm^{-1}) were observed. The carbonyl

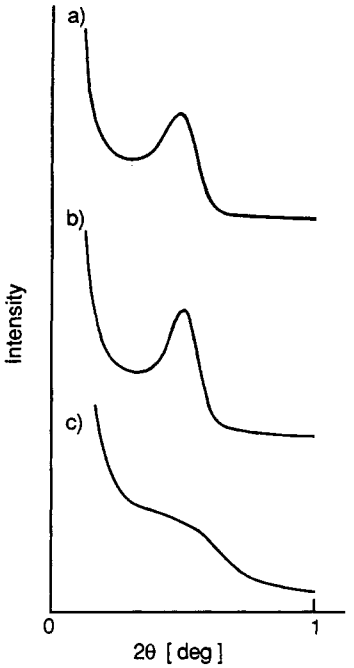

Figure 2. Small-angle X-ray scattering profiles of APS-7/CPEO blend film cast from (a) 1,4-dioxane, (b) benzene, and (c) nitromethane–THF (5/1) (v/v).

absorption band shifted toward lower frequency 1405 cm^{-1} (symmetrical) and 1600–1590 cm^{-1} (antisymmetrical) owing to ionization of the carboxy group although a weak absorption band was still observed at 1744 cm^{-1}. The results indicate that proton transfer from the carboxy group to the amino group occurs partly between polymer chain terminals in the blend system.

Small-Angle X-ray Scattering (SAXS) Measurement of the Polymer Blend. APS was found to be bound to CPEO in the blend through the interaction between amino and carboxy groups at the terminals although the stoichiometry of the complexation has not been confirmed yet. Russell et al. previously reported that the blend of α,ω-dicarboxylic acid poly(α-methylstyrene) and α,ω-bis(dimethylamino)polyisoprene had a microphase-separated structure.[10] Similarly, the complex of APS and CPEO would also be expected to have the ordered structure, which was examined by SAXS measurement. A typical scattering profile of the polymer blend of APS and CPEO cast from benzene was shown in Figure 2b. As can be seen, a scattering maximum was clearly observed corresponding to a Bragg spacing of 170 Å, whereas CPEO, APS, and the blend of homopolystyrene with CPEO gave no scattering maximum. These results suggest that the cross-interaction between amino and carboxy end groups induced the periodic structure in the polymer blend.

The polymer blend (APS-7/CPEO) films cast from various solvents were measured by SAXS to reveal the effect of the cast solvent on the ordered structure. The polymer blend films cast from preferential solvents for polystyrene, 1,4-dioxane (Figure 2a) and ethylbenzene, gave relatively sharp scattering maxima at a Bragg spacing of 180 ± 10 Å. Similar results were obtained from the specimens cast from good solvents for both telechelics, benzene (Figure 2b) and THF. In contrast, the blend film cast from a nitromethane/THF mixture, a preferential solvent for PEO, gave a broad shoulder in the SAXS profile, suggesting that the periodical structure was significantly disordered (Figure 2c). These results suggest that the solubilities of APS and CPEO in the casting solvent reflect the ordering process of the blends. Furthermore, CPEO

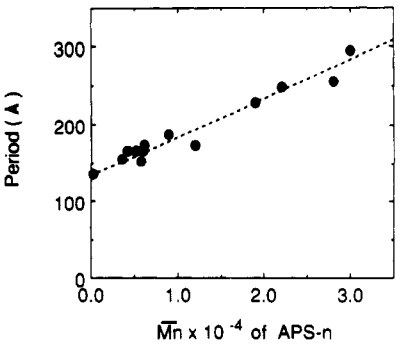

Figure 3. Effect of molecular weight of APS-n (n = 1–14) on the period of the polymer complex.

is crystallized rapidly in various conditions whereas APS produced via anionic mechanism is amorphous. Therefore, the ordering process may be speculated as follows: The crystallization of CPEO occurs first in the ordering process, resulting in the highly ordered structure when a selective solvent for APS or a good solvent for both telechelics is used as a casting solvent. In a preferential solvent for CPEO, on the other hand, the domain of tightly coiled polystyrene is formed first and is followed by the crystallization of CPEO, resulting in lower regularity in the structure.

The effect of the molecular weight of APS on the period of the ordered structure induced in the polymer blend was furthermore studied by SAXS measurement. Film specimens were cast from a benzene solution of APS/CPEO blends including equimolar amounts of ionic groups. The scattering maxima were observed clearly in all cases except for the APS-15/CPEO system where APS-15 had the highest molecular weight, 76 000, in the series of APS. As described later, TEM of the APS-15/CPEO blend showed very wide spacing and irregularity of the structure, which seem to be the reasons for no significant SAXS scattering. Russell et al. reported the results of SAXS measurement for the blend of tertiary amino functionalized polyisoprene with carboxy-terminated poly(α-methylstyrene) where the M_n of the latter were 5000, 10 000, and 15 000. The relationship between M_n of poly(α-methylstyrene) and the period was ambiguous because sphere, cylinder, and lamellar structure might form in the respective blend. Since lamellar structure exclusively formed in all blends studied here, as was described later, an apparently simple relationship was observed between the period of the ordered structure and the M_n of APS, as shown in Figure 3. Obviously, the period measured by SAXS monotonously increased with an increase of the M_n of APS. However, the precise relationship between the period and M_n could not be clearly interpreted in the molecular level at this stage.

TEM Observation of the APS/CPEO Blend. The periodical structure in the polymer blend of APS and CPEO was confirmed by SAXS measurement. Furthermore, transmission electron microscopy (TEM) was carried out with the samples used in the SAXS measurement in order to clarify the morphological structure of the blend. Figure 4 shows the electron micrographs of the thin cross-sectioned blends of APS-5, -11, -14, and -15 with CPEO. In all cases, lamellar layers were observed, where the black part was the PEO domain stained by RuO_4 and the gray one was the polystyrene domain. The periodicity of the layers in TEM seems to correspond to the SAXS data. However, the TEM data could not be quantitatively compared with the results of SAXS since the visual data might not reflect the absolute values of the periods accurately due to slight deformation of the TEM specimen

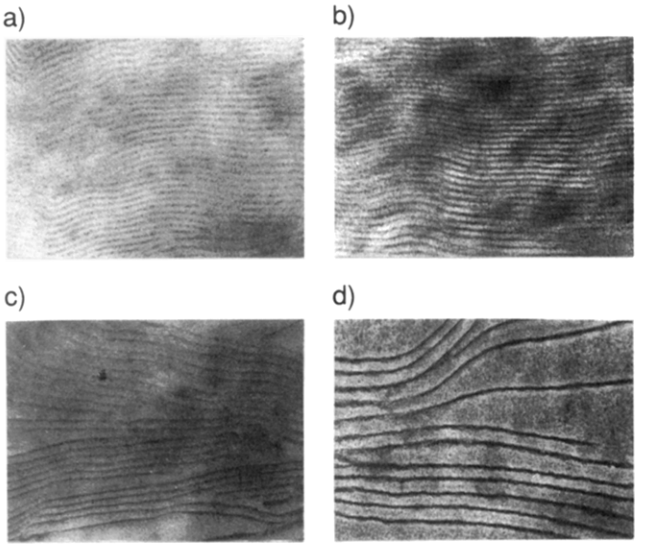

Figure 4. Transmission electron micrographs of the polymer complexes with CPEO (cross section); (a) APS-5; (b) APS-11; (c) APS-14; (d) APS-15. Scale bar indicates 100 nm.

during the sampling process.

According to Molau's law,[14] various forms of microphase-separated structure are induced in amorphous block copolymers, i.e. spheres, cylinders, and lamellae, depending upon the fractional composition, 0–20%, 20–35%, and 35–50%, respectively. In the strong interaction limit, cylindrical or spherical morphology would be induced for the blends of APS-11, -14, and -15 with CPEO, where the contents of CPEO are 31, 22, and 10 wt %, respectively. However, lamellar layers were exclusively observed for these blends as well as that of APS-5 and CPEO (CPEO content, 42 wt %), as shown in Figure 4. Cylindrical structure seemed not to be included because any specimen cross-sectioned perpendicularly to the film surface always showed parallel stripes due to layer structure. Similarly, Kawai et al. reported microphase-separated structure against Molau's law with an ethylene oxide/isoprene block copolymer.[11] In the block copolymer films cast from ethylbenzene, only lamellar structure was observed although the fractions of PEO segment were 23 and 75%. They explained that formation of a folded crystalline sheet of PEO segment prior to microphase separation led to lamellar structure regardless of the segment fraction. Accordingly, it might also be suggested in this study that the crystallization of CPEO occurs before microdomain formation, resulting in the lamellar structures for all blends. As described later, PEO segments in the blends were confirmed to be highly crystallized.

As shown in Figure 4c,d, the lamellar structure did not occupy the whole area in cases of the blends with higher molecular weights of APSs. It might be suggested that the ordering process was not completed during film casting from benzene.

Clear lamellar structures observed by TEM in this study were limited to the shallow part (2–3 μm) at the top surface of the blend film on account of difficulties in staining and microtoming procedures. Poor penetrating ability of RuO_4 into the blend film caused partial stain and fixation in the very shallow part at the top surface. Furthermore, microtoming was very difficult without staining the sample in advance because CPEO in an ultrathin film dissolved in water. Thus, the whole ultrathin section could not be observed by TEM. Hence, SEM observation was alternatively attempted to investigate the structure throughout the cross section of the blend film.

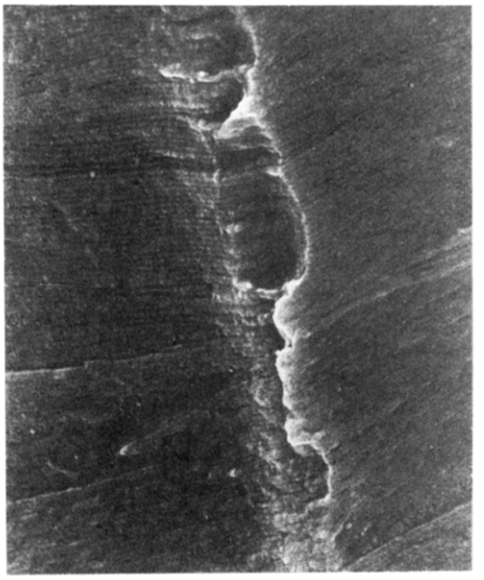

Figure 5. Scanning electron micrographs of the polymer complex (APS-9/CPEO (cross section). Scale bar indicates 200 nm.

SEM Observation of the APS/CPEO Blend. Usually, it is not easy to observe the microdomain directly by SEM because intensities of secondary electrons from the separated domains do not give good contrast. However, Gallot et al. previously succeeded in SEM observation of a microphase-separated structure of a block copolymer containing a crystallized chain of poly(ethylene oxide) using the freeze-fracture technique.[15] Thus, we also tried the direct observation of a fresh fracture of the polymer blend of APS-9 with CPEO by SEM. As shown in Figure 5, beautiful lamellar layers were fortunately observed everywhere in the section. The period, 180 Å, of the lamellae estimated from the picture is in good agreement with the result by SAXS, 190 Å. This may suggest that the regular layer structure was formed in the whole part of the blend system in the case of a lower M_n of APS although the structure was partly disordered in the case of a higher M_n of APS, as was observed by TEM. The very clear layer structure can be seen in the SEM of CPEO/APS, as shown in Figure 5, whereas no periodic structure was found in the SEM of the CPEO film cast from benzene, indicating that the ordered lamellae (Figure 5) were the structures characteristic of the polymer blend of CPEO with APS.

WAXS and DSC Measurements. The results of SAXS, TEM, and SEM studies suggest that the crystallization of CPEO plays an important role in inducement of ordered structure. Hence, WAXS and DSC measurements were here performed to clarify the structure of CPEO lamellae in the blends cast from benzene. The WAXS profiles were shown in Figure 6. The APS-7 film gave the halo owing to the amorphous structure (Figure 6a). In the WAXS profile of CPEO (Figure 6b), reflections of the crystalline part were observed in the region of 15–30° on the amorphous background (shaded area), indicating that CPEO had the $^7/_2$ helical structure similar to the case of PEO.[16] From the area fraction of the crystalline part, the degree of crystallinity of CPEO as-cast film was estimated to be 86%, as shown in Table II. DSC measurement afforded almost the same crystallinities for CPEO and APS-7/CPEO blend films as that of CPEO from the WAXS measurement. Furthermore, the blend film of APS-7/CPEO exhibited the same WAXS pattern (Figure 6c) as that of CPEO. These results may suggest

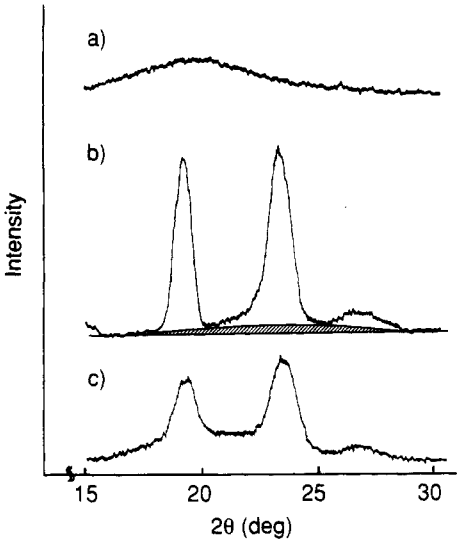

Figure 6. Wide-angle X-ray scattering profiles; (a) APS-7; (b) CPEO; (c) APS-7/CPEO blend.

Table II
Crystallinity of CPEO in Bulk and in the Polymer Complex

sample	T_m, K	ΔH, kJ/mol	crystallinity, % DSC[a]	crystallinity, % WAXS
CPEO in bulk	334	7.5	87	86
CPEO in polymer complex (APS-7/CPEO)	327	7.6	88	

[a] Estimated by (heat of fusion of CPEO)/(heat of fusion of completely crystalline poly(oxyethylene), 8.66 kJ/mol[b]) × 100. [b] Wunderlich, B. *Crystal Melting*; Macromolecular Physics, Vol. 3; Academic: New York, 1980.

that the structure of CPEO lamellae in the blend is similar to that of the CPEO crystal itself.

The melting point (T_m) and glass transition temperature (T_g) of the CPEO/APS blend were measured by DSC at 60 °C and at around 92 °C, respectively, which were almost same as the T_m of CPEO and the T_g of APS. These results indicate that the CPEO crystalline domain and APS domains are segregated and not compatibilized at the molecular level in the blend system.

XPS Measurement. The polymer complex formation may be also confirmed by surface analysis of the APS/CPEO blend using the angular-dependent XPS technique because the surface is a specific area for phase separation. In case of weak interaction between end groups, phase separation occurs and the component of lower surface energy would cover the surface in the macroscale. On the contrary, if the APS/CPEO blend behaves like a block copolymer owing to the strong interaction, a microphase-separated structure might be observed by XPS.

For all specimens, carbon signals from APS and CPEO and the oxygen signal from CPEO were observed in the ESCA spectra. However the nitrogen signal was not detected due to the low content (<0.2 atom %). Figure 7 shows the oxygen content detected by angular-dependent XPS measurement for polymer blends of APS-6 (■) and -10 (△) and homopolystyrene (PS) (●) with CPEO, where the respective oxygen contents in bulk were calculated to be 18.9, 12.9, and 20 atom % on the basis of the mixing ratio. For the PS/CPEO blend, a few percent of oxygen was detected regardless of the takeoff angle. This suggests that the surface within the uppermost ~100 Å is covered

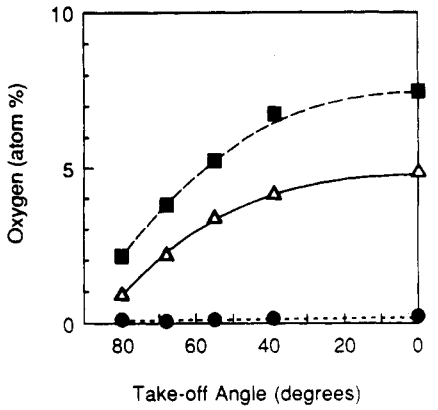

Figure 7. XPS angular dependence of the oxygen signal: (■) APS-6/CPEO blend; (△) APS-10/CPEO blend; (●); polystyrene (M_n = 5100) without amino group/CPEO blend.

almost with a homopolymer of styrene. Because PS has no interacting end group with CPEO, macrophase separation occurred to result in enrichment of the PS of the lower surface free energy (36 dynes/cm) at the surface and in burying the PEO (44 dynes/cm) inside. On the other hand, the oxygen contents of the blends of APS/CPEO increased monotonously with effective sampling depth and reached about 40% of the bulk value at 0° takeoff angle. The data show that the APS layer is enriched within the uppermost several tens of angstroms and that the CPEO domain also comes up to the next several tens of angstroms owing to the intermolecular interaction of $-NH_2/-COOH$ at the chain ends without macrophase separation.

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