

Solubilization of poly(ethylene oxide) into a rod-coil polymer of ethyl 4-[4'-oxy-4-biphenylcarboxyloxy]-4'-biphenylcarboxylate-block-poly(ethylene oxide)

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Solubilization behaviour of poly(ethylene oxide)s (PEOs) (MW = 200–1000) into a rod-coil polymer of ethyl 4-[4'-oxy-4-biphenylcarboxyloxy]-4'-biphenylcarboxylate with poly(ethylene oxide) at a degree of polymerization of 12 (BCEO-12) was studied by using small angle X-ray scattering (SAXS). PEOs were partially miscible with the PEO block of the rod-coil copolymer whether the rod-block of BCEO-12 was crystalline or liquid-crystalline. The amount of PEO which could be solubilized into a domain of coil block decreased on increasing the molecular weight of the added PEO. The solubility limit of PEO increased remarkably when the rod block of BCEO-12 was molten to form a smectic-A phase. This indicated that the solubility limit also increased on reducing the grafting density of coil block. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The morphology and phase behaviour of rod-coil polymers, whose main chain consists of rigid rod-like blocks coupled to flexible coil-like blocks by covalent bonding, have been studied both experimentally and theoretically^{1–4}. As in coil-coil block copolymers, the chemical incompatibility between rod and coil blocks drives them to phase separate. Furthermore, the rigidity and high aspect ratio of rod segments may allow them to assemble with orientation, which leads to the formation of various mesophase on changing temperature.

In our recent paper, we have reported the synthesis of a rod-coil polymer based on poly(ethylene oxide)⁵. We have also reported that a rod-coil polymer of ethyl 4-[4'-oxy-4-biphenylcarboxyloxy]-4'-biphenylcarboxylate with poly(ethylene oxide) with degree of polymerization of 12 (BCEO-12) has a monolayer lamellar structure with alternating rod- and coil-rich domains⁶. At room temperature, a rod-block of BCEO-12 was crystalline and at an elevated temperature transformed into a smectic-A phase. The flexible chains can be considered as grafted polymer brushes while the rod blocks are considered as a solid surface^{7,8}. The chains are mainly stretched along the normal to the rod block, and the fraction of grafted sites depends on the way of packing the rods.

In the present work, we present solubilization behaviour of poly(ethylene oxide)s (MW = 200–1000) into BCEO-12. Poly(ethylene oxide)s having similar chemical

structure with the coil block of BCEO-12 might be solubilized in the domain formed by coil blocks, thereby the lamellar spacing of BCEO-12 was increased. This was studied mainly by measuring changes in lamellar spacings of the mixtures by means of SAXS at various temperatures.

EXPERIMENTAL

BCEO-12 has the chemical structure shown in *Figure 1* and was synthesized and characterized by using the described procedure⁵. PEOs with molecular weight of 200, 600 and 1000 were purchased from Aldrich, and were used as received. Mixtures were prepared by mixing equal weights of PEOs and BCEO-12 under vigorous stirring at temperature above crystal-smectic-A transitions of BCEO-12 in nitrogen atmosphere.

Several experimental techniques were used to study and characterize the BCEO-12/PEOs mixtures. Optical microscopy of mixtures was performed under crossed polarizers to investigate the liquid crystalline phase of the mixture. Optical micrographs were taken at magnifications of 104× using a ZEISS MC100 with Leitz hot stage. Perkin-Elmer DSC-7 differential scanning calorimeters were used to determine the thermal transitions. In all cases heating and cooling rates were 20°C min⁻¹.

X-ray scattering measurements were performed in transmission mode with Ni-filtered Cu K_α radiation supplied by a Rigaku-Denki generator operating at 40 kV and 40 mA. In order to investigate structural

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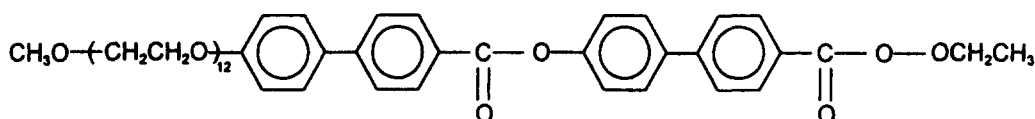


Figure 1 Chemical structure of BCEO-12

changes on heating, a heating stage with an electric heater was used. To prevent molten samples from flowing down, they were sealed with a window of $8\ \mu\text{m}$ thick Kapton film on both sides and the scattering intensity from the Kapton window was subtracted. The SAXS measurement was performed with a Kratky camera fitted with a M. Braun linear position sensitive detector. The correction for the slit-length smearing was applied by means of Strobl's algorithm⁹.

RESULTS AND DISCUSSION

Figure 2 shows d.s.c. traces of the heating scans of pure BCEO-12 and BCEO-12/PEO mixtures. Every thermogram shows glass transition of rod-blocks of BCEO-12 at about 75°C on heating. BCEO-12 exhibits a crystalline melting of the rod block at 125°C and a phase transition from smectic A to isotropic phase at 145°C . BCEO-12/PEO mixtures exhibit a rather broad endothermic peak. From the cooling data of d.s.c. and optical microscopic observations, it was confirmed that these endothermic peaks arose from the melting of crystalline rod-block of BCEO-12 followed by isotropization. The melting temperature of the rod block of BCEO-12 and isotropization temperature were lowered on addition of PEO. We should note that the addition of the lower molecular weight PEO resulted in a much more pronounced lowering of transition temperature.

Figure 3 shows an X-ray diffraction pattern of a BCEO-12/PEO200 mixture taken at indicated temperatures. A wide angle diffraction pattern of the mixture was the same as that for the pure BCEO-12, indicating that the added PEO does not interact with the rod block of BCEO-12. The small angle peaks representing lamellar morphology, however, moved to a lower angle by the addition of PEO200. It means that mixed PEOs are solubilized only into the coil-block. As the temperature

increased up to 107°C , crystalline rod-block melted into the smectic A phase consistent with optical microscopic observations.

The SAXS diffractograms of pure BCEO-12 and BCEO-12/PEO200 mixture taken at indicated temperatures are reproduced in Figures 4 and 5, respectively. Both BCEO-12 and its mixture exhibit the first, second and third order reflections at scattering vector q ($= 4\pi \sin \theta / \lambda$) at a ratio of $1/2/3$. Comparison of the peak positions with the calculated length of a fully extended rod-coil molecule of *ca.* $6.9\ \text{nm}$ suggested that both BCEO-12 and its mixture have a monolayer lamellar morphology. However, the interlamellar spacing of the mixture was larger than that of pure BCEO-12. This increase in lamellar spacing may result from the solubilization of PEO200 into the coil-block of BCEO-12.

As temperature increased from room temperature to the melting temperature of a rod-block of BCEO-12, lamellar spacing increased slightly by thermal expansion. At the melting temperature of a rod block of BCEO-12, lamellar spacings of the pure BCEO-12 and its mixture decreased. However, the reduction in the interlamellar spacing of the pure BCEO-12 was much more pronounced. The decrease of interlayer spacing upon transition from crystalline lamellar to smectic phase was understood by the following speculation. The melting of the rod block causes the packing density of the rod to lower, which results in increasing the average inter-rod distance and rod-coil interfacial area, and reducing coil stretching in order to maintain a uniform density. Consequently, the layer thickness of the coil block decreases. The lowering of the packing density of the rod also gives a similar effect of lowering the grafting density of the coil.

As temperature increased to the isotropization temperature, the peaks disappear more or less completely.

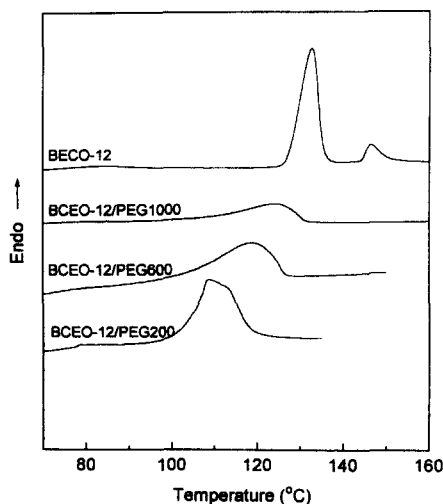


Figure 2 D.s.c. thermograms of BCEO-12/PEO mixtures on heating. The number after the PEG denotes its molecular weight

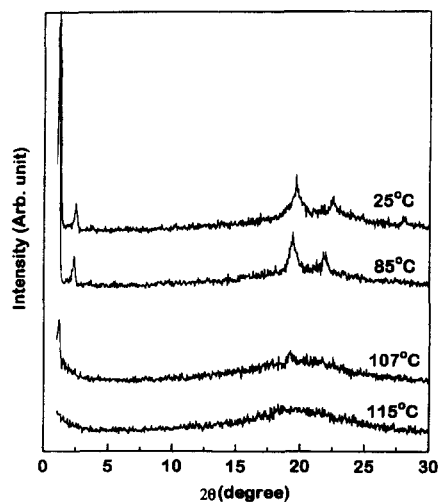


Figure 3 Wide angle X-ray diffractogram of a BCEO-12/PEO200 1/1 (w/w) mixture taken at indicated temperatures

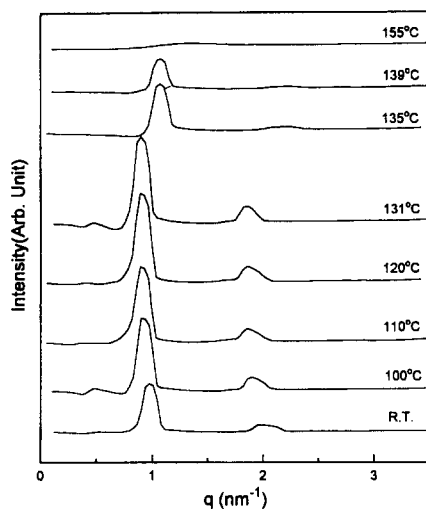


Figure 4 Small angle X-ray diffractogram of BCEO-12 taken at indicated temperature. The scattered intensity in arbitrary units is plotted against the scattering vector $q (= 4\pi \sin \theta / \lambda)$, where 2θ and λ are the scattering angle and the wavelength of the X-ray, respectively

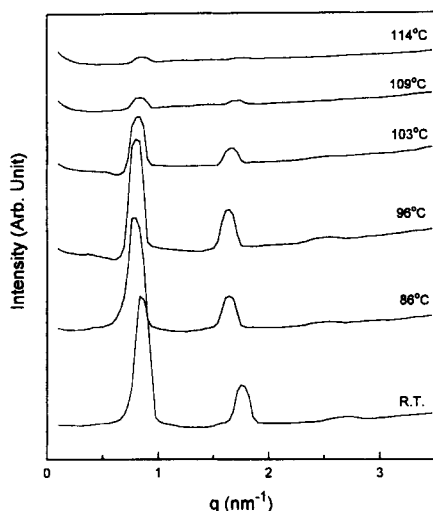


Figure 5 Small angle X-ray diffractogram of a BCEO-12/PEO200 mixture taken at indicated temperatures

However, the intensity curve still exhibits a small broad peak at about the same scattering vector as the main peak obtained at lower temperatures. The presence of a small peak is not due to a persistence of microdomain structure but the effect of the correlation hole in the disordered phase of block copolymer^{10,11}.

To investigate how much PEOs can penetrate, the increments in lamellar spacing were measured for the other mixture at a 3/7 (w/w) BCEO-12/PEO200 ratio. The mixture exhibited the same increments as the 1/1 (w/w) mixture, even though the mixture ratio had been changed remarkably. This constant increment indicated that an excess of PEO was added to BCEO-12 and a solubility limit existed in the mixture systems. Here the solubility limit is defined by saturated volume fraction of PEOs penetrated into the coil-block against the total volume of the miscible phase of the mixture.

SAXS experiments have been performed for the other mixtures having PEOs of different molecular weight. Since other mixtures showed similar features to the

mixture, only the interlamellar distance is reproduced as a representative example. *Figure 6* shows reproduced temperature dependencies of lamellar spacing of pure BCEO-12 and BCEO-12/PEO mixtures.

To determine the solubility limit value out of the lamellar spacing values measured experimentally, a simple geometrical calculation is taken into account. Let the solubility limit ϕ_k be defined as

$$\phi_k = \frac{V_k}{V_T} \quad (1)$$

where V_k is the saturated volume of PEOs dissolved in the coil-block and V_T the total volume of the miscible phase of the mixtures. Volume in equation (1) can be converted into length since all of the mixtures have the same monolayer lamellar morphology. In *Figure 6*, ϕ_k values of PEOs evaluated for mixtures at 25°C and smectic phase are plotted. As *Figure 7* shows, ϕ_k decreases with increasing molecular weight of PEOs.

The dependence of molecular weight and grafting density on the solubilization may be qualitatively

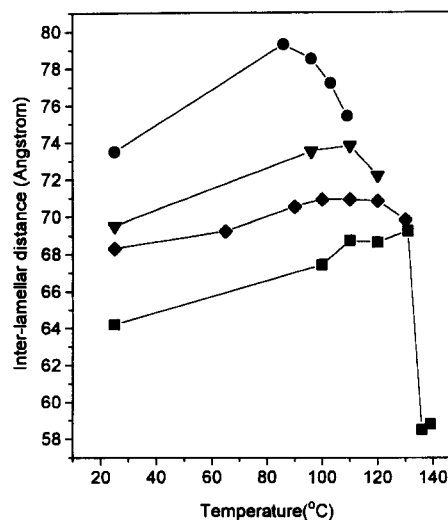


Figure 6 Temperature dependence of lamellar spacing of pure BCEO-12/PEO mixtures on heating: (■) BCEO-12; (◆) BCEO-12/PEO1000; (▼) BCEO-12/PEO600; (●) BCEO-12/PEO200

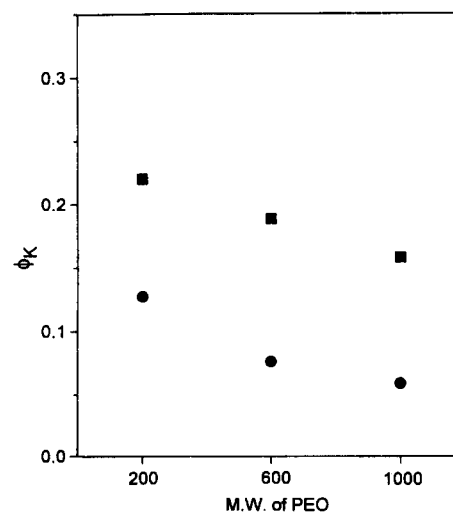


Figure 7 Solubility limit of PEOs evaluated for mixtures at 25°C (filled circles) and smectic phase (filled squares)

understood as follows: among several factors mixing entropy of mobile polymer and elastic entropy changes of grafted chains may be the dominant factors determining the solubility limit of poly(ethylene oxide) into the grafted oligo(ethylene oxide) chains. The mixing entropy is a driving force for the solubilization, whereas the increase of elastic energy on mixing limits the solubilization. Free energy change associated with the solubilization may be given by

$$\Delta G_{\text{solubilization}} = \Delta G_{\text{mixing}} + \Delta G_{\text{elastic}} \quad (2)$$

with

$$\frac{\Delta G_{\text{mixing}}}{kT} \propto \frac{\phi_s \ln \phi_s}{M_s} \quad (3)$$

and

$$\frac{\Delta G_{\text{elastic}}}{kT} \propto \left(\frac{L_{\text{after_mixing}}^2}{R_0^2} \right) - \left(\frac{L_{\text{before_mixing}}^2}{R_0^2} \right) \quad (4)$$

where ϕ_s and M_s are the fraction and the molecular weight of a mobile polymer, respectively. L and R_0 are the end-to-end distances of stretched and unperturbed grafted chain, respectively. Since ΔG_{mixing} is inversely proportional to the molecular weight of the mobile polymer, the decrease in the solubilization with increasing molecular weight of PEOs is qualitatively explained.

When the chains are strongly stretched along the normal to the layer such as in this system, the end-to-end distance of the grafted chain may be linearly proportional to the thickness of the layer. The decrease of interlayer spacing of the pure BCEO-12 upon transition from crystalline lamella to smectic phase implies the reduction of the elastic energy. With mixing of the same amount of the mobile polymer, the increase in the elastic

energy of the grafted chain in the smectic phase is less pronounced than that in the crystalline phase. Therefore, the increase in the solubility limit is expected upon transition as shown in this experimental result.

In conclusion, PEOs were miscible with the coil blocks of BCEO-12. The lamellar structure was not disrupted by adding PEOs and on adding excess PEOs the presence of solubility limit was confirmed. With increasing molecular weight of PEOs, the solubility limit of PEOs decreased and the solubility limit of PEOs increased remarkably as the rod-block of BCEO-12 melted into the smectic-A phase.

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