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NANO-SCALE STRUCTURE CHANGE OF AMPHIPHILIC DI-BLOCK COPOLYMER BY BLEND

S. Y. Jung[1]* *and H. Yoshida*[2,3]

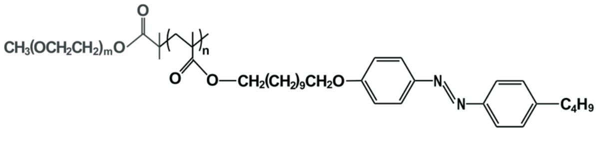
[1]Tokyo Metropolitan University, Graduate School of Engineering, Department of Applied Chemistry, 1-1 Minami-osawa, Hachiouji, Tokyo 192-0397, Japan
[2]Tokyo Metropolitan University, Faculty of Urban Environments, Department of Applied Chemistry, 1-1 Minami-osawa, Hachiouji, Tokyo 192-0397, Japan
[3]CREST(JST)

The phase transition and nano-scale ordered structure of four types of blends prepared from four di-block copolymers, consisting of hydrophilic poly(ethylenoxide) and hydrophobic poly(methacrylate) derivative, PEO_m-*b*-$PMA(Az)_n$ having different PEO molecular length and same degree of polymerization of PMA(Az) were investigated. All blend systems formed hexagonal packed PEO cylinder structure, which was same with the nano-scale structure of these parent block copolymers. The SAXS and AFM observation suggested that the size of hexagonal structure of blend was larger than the average size of parent block copolymers. The melting enthalpy of PEO in blends was larger than the average value of parent block copolymers. DSC, SAXS and AFM observations indicated the miscible blend systems.

Keywords: *AFM, blend, di-block copolymer, hexagonal packed cylinder, melting enthalpy, micro-phase separation, SAXS*

Introduction

Block copolymers form the nano-scale ordered structures such as spheres, cylinders, bi-continuous gyroid, lamellae morphologies, as the results of repulsive interaction between copolymer components depending on the relative volume fractions of components and temperature [1, 2]. We have reported the nano-scale ordered structure and phase transitions for amphiphilic di-block copolymer consisted of hydrophilic poly(ethylene oxide) and hydrophobic poly(methacrylate) having azobenzene moieties in ester groups (PEO_m-*b*-$PMA(Az)_n$) as shown in scheme 1 [3–5]. The amphiphilic di-block copolymers PEO_m-*b*-$PMA(Az)_n$, in which the subscripts m and n indicate the degree of polymerization of hydrophilic and hydrophobic sequences, respectively, form the ordered hexagonal packed PEO cylinder structure selectively in the wide ranges of both copolymer fraction and temperature [3–5]. PEO_m-*b*-$PMA(Az)_n$ shows four-phase transitions in both hydrophilic and hydrophobic domains including melting, liquid crystalline transition and isotropic transition [3, 5].



Scheme 1 Molecular structure of PEO_m-*b*-$PMA(Az)_n$ block copolymer

On the other hand, we have reported that the size of ordered structures formed by PEO_m-*b*-$PMA(Az)_n$ was controllable by blending of PEO homopolymer [6]. The di-block copolymer, PEO_{114}-*b*-$PMA(Az)_{24}$, and homopolymer, PEO_{114}, are miscible in molecular level in the PEO mass fraction range up to 60% from the results of isothermal crystallization and the lattice spacing changes of (100) and (110) planes of hexagonal nano-scale structure which increase linearly with PEO fraction [6]. Hashimoto *et al*. [7–9] reported the ordered microdomain structure of binary mixtures of poly(styrene-*b*-isoprene) di-block copolymer (SI), a weak segregated system, and homopolystyrene (PS) as a function of molecular mass of PS (M_{homo}). The interdomain distance formed by SI increases with the increase of M_{homo}, and the morphological transition from cylinders to lamellae is observed by blending PS with high M_{homo}. The lamellar morphology in binary blends of SI and PS with various molecular masses have been investigated by Winey *et al*. [10–11]. In the SI/PS blends, the polystyrene layer thickness increases and the polyisoprene layer thickness decreases with the increase of PS concentration. Izuka *et al*. [12] reported the formation of nano-colloidal spheres in blend of poly(vinyl methyl ether) and SI. The self-assembled patterns of the binary mix-

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* Author for correspondence: jung-sunyoung@c.metro-u.ac.jp

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tures of poly(2,6-dimethylphenylene oxide) and SI are reported by Hasshimoto *et al*. [13]. The blend with homopolymers influences the nano-scale structures of weak segregated di-block copolymers such as SI, because the relative volume fractions of system changes by blend without the change of molecular interaction between copolymer components.

In this study, we investigated the nano-scale ordered structure and the phase transitions for the blends of amphiphilic di-block copolymers, PEO_m-*b*-$PMA(Az)_n$, having same molecular length of PMA(Az) sequence and different molecular length of PEO sequence to discuss the effect of PEO fraction on the nano-scale structure of blend systems.

Experimental

Parent block copolymers used for copolymer blends were four amphiphilic di-block copolymers prepared by the atom transfer radical polymerization method from different molecular mass of PEO, PEO_{454}-*b*-$PMA(Az)_{43}$ (P454; Mw/Mn=1.05), PEO_{272}-*b*-$PMA(Az)_{40}$ (P272; Mw/Mn=1.07), PEO_{114}-*b*-$PMA(Az)_{40}$ (P114; Mw/Mn=1.08) and PEO_{40}-*b*-$PMA(AZ)_{39}$ (P40; Mw/Mn=1.10), having same degree of polymerization of PMA(Az). Four kinds of blend samples, P454/P272, P272/P114, P114/P40 and P272/P114/P40 were prepared by solvent casting from toluene solution of parent block copolymers. Blends were annealed at 140°C for 24 h to form the equilibrium nano-scale ordered structure. All blends were prepared as a molar equivalent system. The PEO mass fraction (ϕ_{PEO}) of parent block copolymers and blend systems were 48.7 (P454), 38.0 (P272), 20.6 (P114), 8.8 (P40), 43.4 (P454/P272), 29.3 (P272/P114), 22.6 (P272/P114/P40) and 14.8 (P114/P40) %.

Differential scanning calorimetry (DSC)

The phase transition behaviors were investigated by a differential scanning calorimeter (DSC6200, Seiko Instruments Co. Ltd) equipped with a cooling apparatus in dry nitrogen gas atmosphere. The sample mass and scanning rate were 3 mg and 10 K min^{-1}, respectively. The phase transition temperatures of melting and crystallization were employed the on-set temperature at 10 K min^{-1}.

Small-angle X-ray scattering (SAXS)

The SAXS measurements were carried out at the beam line 10C at Photon Factory, High Energy Acceleration Organization, Tsukuba, Japan. The wavelength of monochromatic X-ray (λ) was 0.1488 nm. The distance between sample and detector (PSPC, Rigaku Co. Ltd, 512 channels) was 860 mm, which covered $1.02\ \text{nm} < s^{-1} = q/2\pi = \lambda/2\sin\theta < 60.8\ \text{nm}$, θ was a half scattering angle. The samples for SAXS measurement was annealed at 140°C for 24 h and cooled to –30°C to crystallize PEO sequences.

Atomic force microscope (AFM)

For the observation of nano-scale structure for blends, atomic force microscope (WET-SPM-9500 J3, Shimadzu) measurement was carried out in contact mode equipped with a Veeco-TAP150 tip. The sample for AFM observation was prepared by spin coating of toluene solution on silicon wafer, and was annealed at 140°C for 24 h and cooled to –30°C to crystallize PEO sequences.

Results and discussion

The nano-scale ordered structure for blend samples through micro-phase separation was determined by SAXS. Figure 1 shows the SAXS profiles of parent block copolymers and blend systems. The diffraction peak at q=2 nm^{-1} corresponded to the smectic layer of PMA(Az) domain. The *q* value and intensity of the diffraction peak corresponded to the smectic layer of the blends were almost the same with that of the parent block copolymers. The smectic structure in PMA(Az) domain was scarcely influenced by blending. The diffraction peaks observed at the q range be-

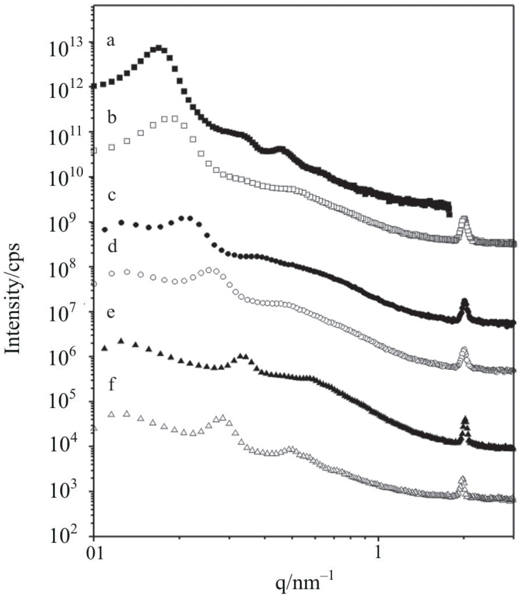

Fig. 1 SAXS profiles of parent block copolymers and blends ; a – P454, b – P454/P272, c – P272, d – P272/P114, e – P114, f – P272/P114/P40

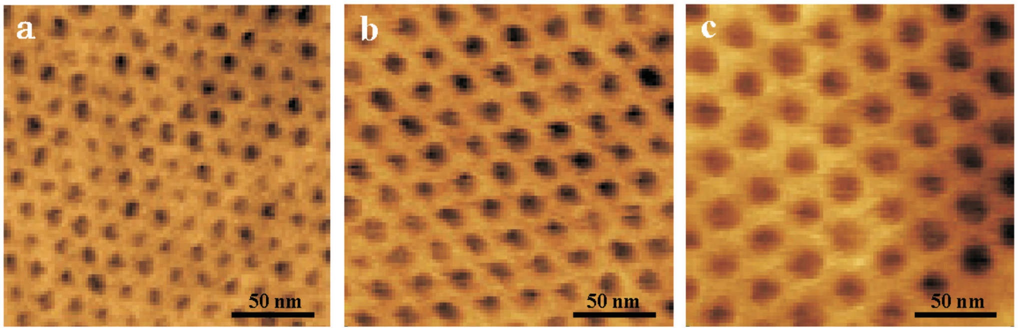

Fig. 2 AFM images of nano-scale ordered structure for blend systems; a – P114/P40, b – P272/P114, c – P454/P272

low 1 nm^{-1} were due to the nano-scale ordered structure. The diffraction peaks with the reciprocal Bragg spacing in the ratio of 1, $\sqrt{3}$,$\sqrt{4}$,$\sqrt{7}$ suggested the hexagonal packed cylinder structure for the parent block copolymers. The blend systems indicated the diffraction peaks in the ratio of 1, $\sqrt{3}$,$\sqrt{4}$ also suggested that the hexagonal packed cylinder structure, however the peaks corresponded to $\sqrt{4}$ and $\sqrt{7}$ became smaller. The diffraction peak of (100) plane of the blends shifted toward the middle of those of parent block copolymers, and the peak width became broader by blending. These results indicated that the blends formed the nano-scale hexagonal packed cylinder structure, however, the order of hexagonal structure slightly decreased by blending.

Figure 2 shows AFM topological images of nano-scale structures for the blends P114/P40 (a), P272/P114 (b) and P454/P272 (c). The black parts corresponded to the top view of hexagonal packed PEO cylinders, which became hollow from hydrophobic PMA(Az) domain. AFM images of blends indicated the top view of high ordered hexagonal packed cylinders structure. The diameter of cylinder and the distance between cylinders increased with the increase of molecular mass of PEO in parent block copolymers, however, the distribution of cylinder diameter became wide in the order of P114/P40, P272/P114 and P454/P272. These AFM results agreed with the results of SAXS measurement.

Figure 3 shows the DSC curves for copolymers P454 and P272 and their blend P454/P272 on the second heating (a) and cooling process (b) at 10 K min^{-1}. In the case of heating DSC profile (a), several endothermic peaks of PEO for parent block copolymers were observed. The endothermic peaks at 70 and 125°C were due to the melting and the isotropic transitions in PMA(Az) domain. The endothermic peaks observed in the range between 40 and 60°C corresponded to the melting of PEO. The PEO melting peak of P454 and P272 accompanied with the shoulder at the lower temperature side, and the double melting peaks were observed at 53 and 57°C for

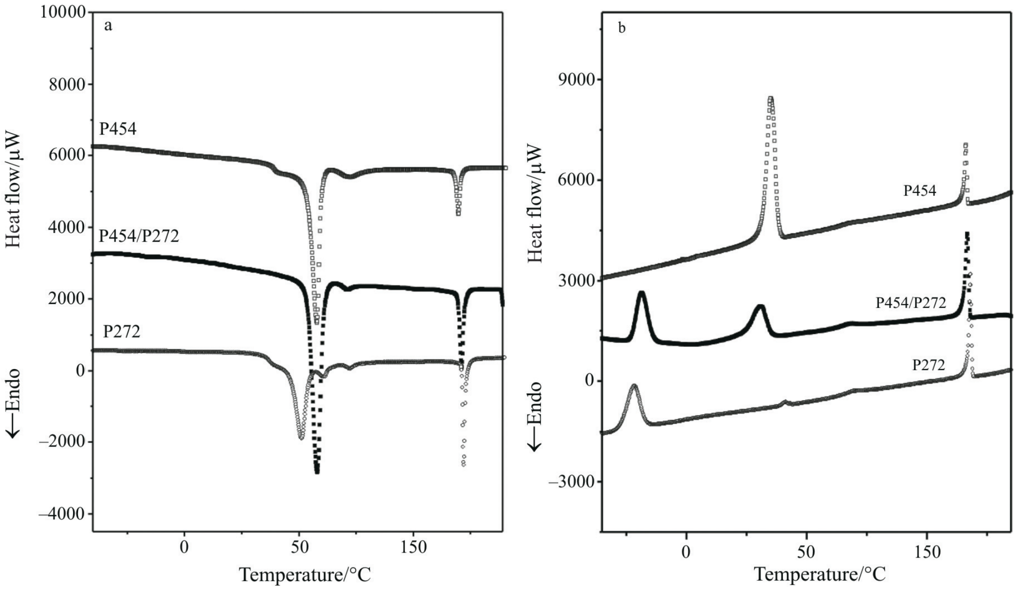

Fig. 3 DSC curves of parent block copolymers P454, P272 and blend P454/P272 on a – second heating and b – cooling at 10 K min^{-1}

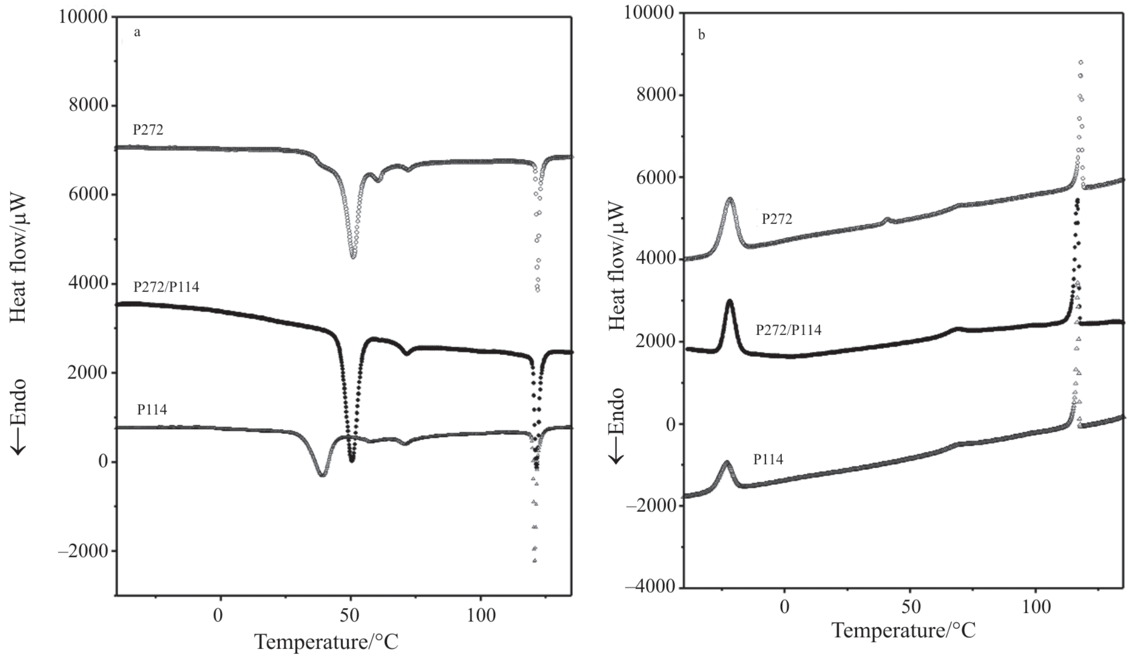

Fig. 4 DSC curves of parent block copolymers P272, P114 and blend P272/P114 on a – second heating and b – cooling at 10 K min^{-1}

P272. The later was same with the melting of PEO for P454. The P454/P272 blend showed three endothermic peaks including two transitions in PMA(Az) domain. The simple melting peak of PEO was observed for P454/P272 blend and was same with the melting of PEO for P454.

On the other hand, three exothermic transitions appeared on cooling DSC curve of P454. The exothermic peaks at 120 and 68°C were the transition from the isotropic liquid to the smectic phase and the crystallization of PMA(Az) respectively. The exothermic peak at 38°C was the crystallization of PEO for P454. P272 showed two peaks of PEO crystalliza-

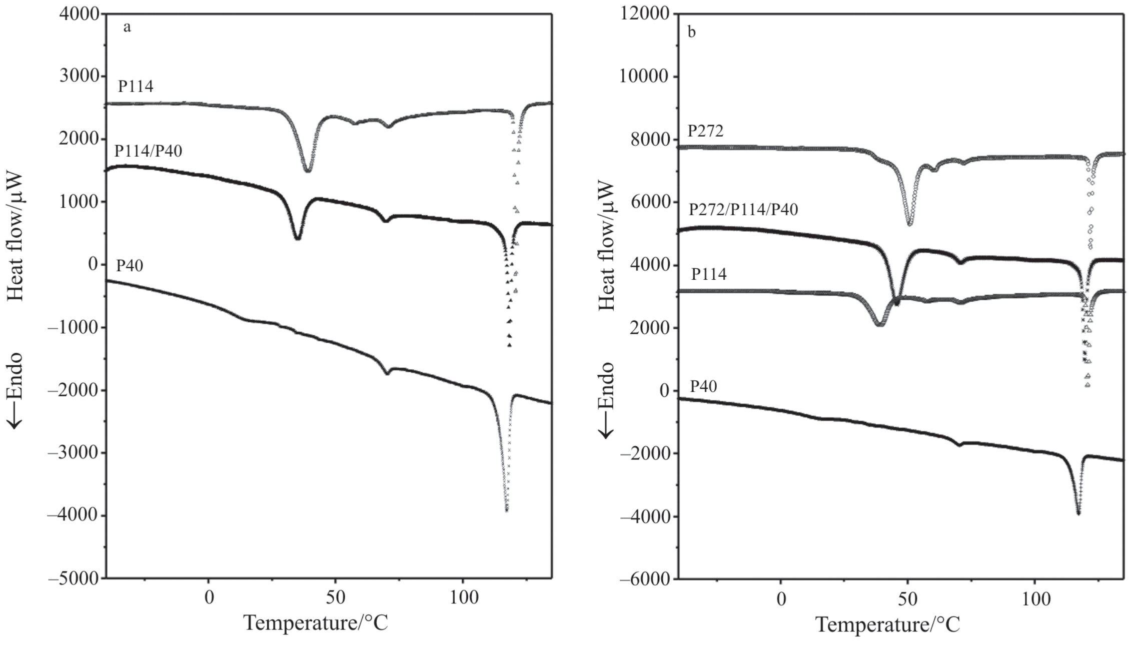

Fig. 5 DSC curves of parent block copolymers and blends on second heating at 10 K min^{-1} a – P114, P40 and blend P114/P40, b – P272, P114, P40 and blend P272/P114/P40

tion at 38 and –20°C on cooling, these two crystallization process produced the crystallites having different stability and gave the double melting peaks. P454/P272 blend showed four exothermic peaks on cooling, the peaks at 38 and –20°C corresponded to the crystallization of PEO sequences in P454 and P272, respectively. However, the exothermic enthalpy normalized by the mass fraction of PEO at –20°C was larger than that of the exothermic peak at 25°C, which indicated that some PEO in P454 of P454/P272 blend crystallized at –20°C. Although two crystallization peaks observed on cooling, one simple melting peak was observed on heating for P454/P272 blend. The melting behavior of P454/P272 blend indicated that PEO sequences of P454 and P272 were miscible in PEO cylinders.

Figure 4 shows the second heating (a) and cooling (b) DSC curves for copolymers P272 and P114 and their blend P272/P114. Although the parent block copolymers P272 and P114 showed the double melting peaks of PEO in the temperature range between 30 and 60°C, their blend P272/P114 showed one simple melting of PEO without the shoulder at the low temperature side. The melting peak of PEO in blend was almost the same with that of P272. On cooling, the crystallization peak of PEO in P272/P114 blend was sharper than that of the parent block copolymers. This result suggested that the crystallization rate of PEO in P272/P114 blend was faster than the parent block copolymers. The crystallization of PEO in di-block copolymer depended on the size of PEO cylinder, the crystallization rate of PEO in small PEO cylinder was slower than that of PEO in large cylinder.

Figure 5 shows DSC heating curves of binary blend P114/P40 (a) and triple blends of P272/P114/P40 (b). P40 showed the small and broad melting peak of PEO at 10°C, because the crystallinity of PEO in P40 was low due to the narrow PEO cylinder. Both binary and triple blends showed the simple PEO melting peak. The PEO melting temperature of binary and triple blends was slightly lower than that of di-block copolymer showing the highest PEO melting.

DSC heating curves of blend systems shown in Figs 3–5, the PEO melting peak for the blend systems was simple and single, and the PEO melting temperature was almost the same with that of parent block copolymer having the higher molecular mass of PEO. These results indicated that the stability of PEO crystal was influenced by the molecular mass of PEO in parent block copolymer, which formed the larger PEO cylinder.

Figure 6 shows the relationship between the PEO fraction (ϕ_{PEO}) and the melting enthalpy of PEO (ΔH_{PEO}) normalized by PEO fraction in both parent block copolymers and blends. P40 gave the lowest ΔH_{PEO} value due to the narrow PEO cylinder less than 5 nm in diameter. P454/P272 showed the average ΔH_{PEO} value of parent block copolymers. The other blends showed larger ΔH_{PEO} than the average ΔH_{PEO} value of their parent block copolymers, which indicated that the crystallinity of PEO in blends was larger than that of parent block copolymers.

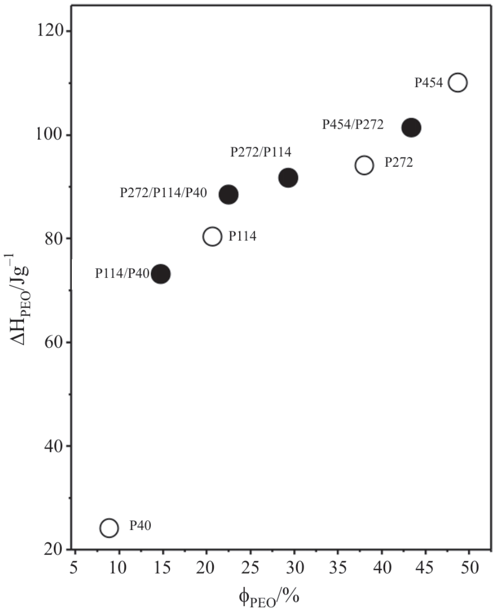

Fig. 6 Relationship between PEO melting enthalpy (ΔH_{PEO}) vs. ϕ_{PEO} ● – PEO fraction for blends and ○ – parent block copolymers

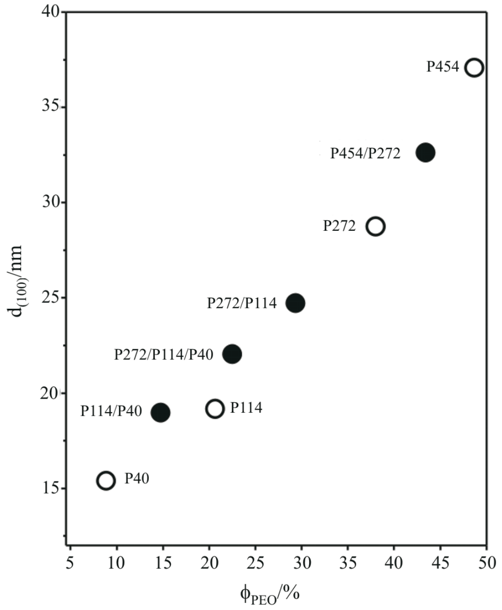

Fig. 7 Relationship between space distance of (100) plane of hexagonal structure *vs.* ϕ_{PEO} ● – PEO fraction for blends) and ○ – parent block copolymers

Figure 7 shows the relationship between the PEO mass fraction (ϕ_{PEO}) and the lattice spacing of (100) plane ($d_{(100)}$) of hexagonal packed cylinder. The P454/P272 blend showed the average value of $d_{(100)}$ of parent block copolymers. The other blends showed the $d_{(100)}$ value larger than the average $d_{(100)}$ value of parent block copolymers. These results suggested that the size of nano-scale structure of blends was influenced by the parent block copolymer having higher molecular mass of PEO, which formed the larger diameter of PEO cylinder.

The results shown in Figs 6 and 7 indicated the PEO sequences of parent block copolymers were miscible in PEO cylinder of blends. Di-block copolymer formed the nano-scale ordered structure with the size of the radius gyration in each component, the diameter of PEO cylinder was strongly influenced by the molecular mass of PEO sequence of block copolymer. In the narrow space, the crystallization process was restricted by the limited molecular motion due to the restrictions from the space and the interface between components. With decreasing the PEO cylinder diameter, these restrictions increased and the crystallization of PEO became difficult. Therefore, P40 showed the smallest ΔH_{PEO} as shown in Fig. 6. By blending di-block copolymers having different molecular mass of PEO (indicating the different PEO cylinder diameter), the blend preferred to form larger PEO cylinder than the average diameter of parent block copolymers in order to accommodate the larger PEO sequences of the parent block copolymer having larger molecular mass of PEO. Therefore, the ΔH_{PEO} values of blends were larger than the average ΔH_{PEO} value of parent block copolymers. These phenomena were the results of miscible blends of parent block copolymers.

Conclusions

Three types of binary and one triple blend systems of amphiphilic di-block copolymers having same molecular length of hydrophobic sequence and different molecular length of hydrophilic sequence were investigated by DSC, SAXS and AFM. All blends formed the hexagonal packed cylinder nano-scale ordered structure similar to those of parent block copolymers, however, the order of nano-scale structure of blends was less than that of those parent block copolymers. The size of hexagonal structure of blends was larger than the average size of nano-scale structure of parent block copolymers. Thermal and structural behaviors suggested that blends were miscible systems.

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