Interchain Hydrogen Bonding Interaction Induced phase Behaviors of Poly(ethylene oxide)-b-poly(N-vinylcarbazole)/Poly(acrylic acid) Blend

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Supporting Information

ABSTRACT: In this paper, we study an αβ/C blend system composed of a diblock copolymer of poly(ethylene oxide)113-b-poly(N-vinylcarbazole)77 (PEO113-b-PVK77) and a homopolymer of poly(acrylic acid) (PAA) with a weight-average molecular weight of 1900 g/mol. The phase behavior of the blend was characterized using various techniques including Fourier transform infrared spectroscopy, differential scanning calorimetry, small-angle X-ray scattering, and transmission electron microscopy. The experimental results indicate that while the PEO and PVK blocks are miscible in bulk state, adding PAA into the diblock can lead to microphase separation of the blend due to the interchain hydrogen bonding complexation between PEO and PAA. The phase morphology of the blend is strongly dependent on the PAA composition. Only with sufficiently high weight fraction of PAA (wtPAA), the blends can present ordered microphase-separated structures, although the long-range order is not well developed. For 40% < wtPAA < 70% (corresponding to the PVK volume fraction between 44% and 22%), the ordered phase is changed from lamella to cylinder to cubic phase with increasing wtPAA. Further increase of PAA content results in spheres with the core of PVK dispersed in the matrix of PAA. The diameters of the PVK cores of cylinders and spheres are very close to the twice of the unperturbed end-to-end distance of the PVK block, indicating that the rather rigid PVK block is hard to be deformed during microphase separation. The PAA composition dependence of the blend phase behavior illustrates that the degree of PEO/PAA complexation dominates the segregation strength. After the microphase separation occurs, the phase morphology can be adjusted by varying the PAA content.

INTRODUCTION

Diblock copolymer composed of two blocks of α and β may exhibit fascinating and complex self-assembly behavior, of which the microphase separation is mainly dependent on the segment–segment interaction parameter (χαβ), the degree of polymerization, and the volume fraction of α block.1,2 When a αβ diblock copolymer is mixed with a homopolymer C, the presence of C introduces additional factors including the interaction parameters of χαC and χβC, the molecular weight (MW) and the volume fraction of C, etc., which may also strongly affect the competitive balance between enthalpic and entropic contributions. Consequently, blending diblock copolymer with homopolymer provides a convenient and efficient route to adjust the phase behavior, which in turns controls properties of the materials. Most of the αβ/C blends studied possess an immiscible αβ diblock copolymer. A simple case of C = α has been widely investigated.3–8 It has been demonstrated that when the MW of C is smaller than that of the α block, the C can act as the stabilizer of the ordered phases, in which some space can be occupied by C instead of being filled by the stretched α blocks; just varying the blend composition may change the domain size and also the morphology of ordered structures.9,10

The situation becomes more complex when the chemical structure of C is different from that of both α and β (C ≠ α ≠ β), wherein the χαC and χβC and the difference between these two interaction parameters become critical.11 Of particular interest is that the C homopolymer can preferentially interact with one block (e.g., α) of the diblock. To make the favorable interaction between the pair of α and C sufficiently strong, one may introduce interchain hydrogen bonding or electrostatic force into the αβ/C system.12–21 This strategy has been confirmed to be rather effective to encourage the αβ/C to undergo microphase separation.14,16 In this case, the C will
selectively mix with the α block, forming α/C-domain within the ordered microphase-separated structures regardless of the MW and the amount of C added, and the morphology of the blend can be tuned accordingly. For a blend system of polystyrene-β-poly(2-vinylpyridine) (PS-b-P2VP) and poly(4-hydroxytert-butylstyrene) (P4HS) which exhibits the interchain hydrogen bonding between P2VP and P4HS, it is found that the increase of MW of P4HS results in a structural transition from hexagonally packed cylinders to lamellae. In a polystyrene-β-poly(4-vinylphenol) (PS-b-P4VP)/poly(4-vinylpyridine) (P4VP) blend, a series of order–order phase transitions are observed, which follows the sequence of lamella–gyroid–hexagonal cylinder–body centered cubic sphere with increasing P4VP content.

Recently, the αβ/C blend with a miscible αβ diblock copolymer has received more attention. Considering that there is strong preference of attractive interaction between α and C, adding C may drive the α block to separate from the β block. Once the reduction in interaction energy due to forming α/C domain dominates the conformational entropy loss, the blend may reduce their free energy through microphase separation. Zhou and Shi theoretically investigated the phase behavior of αβ/C blends where all the three binary pairs, αβ, α/C, β/C are miscible.29 When the pair interactions of α/C and β/C are sufficiently different, a closed-loop of immiscible region exists. Furthermore, different ordered microphase-separated structures can be identified inside the closed-loop. In experiments of the αβ/C blends with a miscible αβ, regular ordered nanostructures have been achieved. For examples, Kuo et al. reported that poly(vinylpyrrolidone)-b-poly(methyl methacrylate) (PVP-b-PMMA)/poly(4-vinylphenol) (PVPPh) blend and PVPPh-b-PMMA/PVP blend systemcan render ordered lamellar or hexagonal phase.12,17,24 In these blends, despite the miscibility of binary pairs, the strong hydrogen bond interaction between PVPPh and PVP makes PVPPh/PVP complex effectively immiscible with PMMA. Very interestingly, for a miscible triblock copolymer αβα, addition of C that selectively hydrogen bonds with α can also produce strong segregation. Watkins et al. reported that blending the low MW disordered triblock copolymers of poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO-b-PPO-b-PEO, Pluronic) with a homopolymer, which can selectively associate PEO such as poly(acrylic acid) (PAA) via hydrogen bonding, could yield well-ordered microphase-separated melts.25,26 With increasing the PAA content, the blend undergoes disorder-to-order transition followed by order-to-order transitions.

In this paper, we study the phase behavior of interchain hydrogen bonding induced microphase separation of poly-(ethylene oxide)-b-poly(N-vinylcarbazole)/PAA (PEO-b-PVK/PAA) blend. PVK with a rather simple chemical structure has attracted great academic and industrial interests for decades.27 Because of its good photoconductivity and hole transport property, PVK plays a significant role in constructing advanced polymeric materials with excellent electrical and optical properties.28 One may expect that microphase-separated PVK diblock copolymers may facilitate the fabrication of PVK-based materials with desired nanostructures, by which one can optimize the electro-optical functions.28,29 Although PVK homopolymer can be obtained readily by different polymerization methods, synthesis of PVK diblock copolymer is a challenging task.30,31 Recently, using a PEO-based xanthate as the macromolecular chain transfer agent, we successfully synthesized a series of PEO-b-PVK diblock copolymer via reversible addition–fragmentation chain transfer (RAFT) polymerization of N-vinylcarbazole monomer.31 However, the PEO-b-PVK we obtained containing the PEO block with a low MW [number-average MW of 5000 g/mol, i.e., degree of polymerization (DP) of 113] is at least partially miscible. Therefore, we intend to obtain the microphase-separated structures with pure PVK domains by blending the homopolymer of PAA with PEO-b-PVK. This blend system belongs to the catalog of αβ/C with a miscible αβ diblock. Since the hydrogen bonding complexation between complementary binding sites on PEO and PAA are pretty strong,32 we expect that the tendency of microphase separation of the blend will be driven by an effective repulsion between PEO/PAA complex and PVK block which originates from a large difference in the attractive interactions between the different blocks.

Here we focus on the blend system of PEO113-b-PVK77 (the numbers refer to the DP of PEO and PVK) and PAA (weight-average MW of 1900 g/mol). Various techniques including Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM) were employed to characterize the phase behavior of the blend system. The experimental results show that adding small amount of PAA causes local density fluctuation. Only after enough PAA is added, the blend can form some ordered microphase-separated structures. When the PAA weight fraction (wPAA) is in the range of 40% < wPAA < 70%, the blend morphology changes from lamella to cylinder to sphere with increasing wPAA. However, the long-range order of the microphase separation is not well developed, which is probably due to the presence of residual homo-PVK chains in the diblock synthesized by RAFT and the PVK domains in the blend are rigid. Adding more PAA results in the spheres with the core of PVK and shell of PEO/PAA complex dispersed in the matrix of PAA. To visualize the assembly structures more clearly, we designed a water etching method to prepare the TEM sample. After the low MW PAA was washed out in water, we observed the cylindrical and spherical domains, with the core dimension of PVK block very close to the twice of PVK’s unperturbed end-to-end distance. The PAA composition dependence of the blend phase behavior illustrates that the degree of PEO/PAA complexation dominates the segregation strength. Moreover, after the microphase separation occurs, varying the PAA content can effectively adjust the phase morphology.

**EXPERIMENTAL SECTION**

**Materials and Sample Preparation.** The diblock copolymer PEO113-b-PVK77 with a polydispersity of 1.11 was synthesized by RAFT method. To remove the residual PVK homopolymer in the polymerization product, the sample was purified by fractionation. The detailed synthetic route and characterization of the diblock copolymer was reported elsewhere.31 PAA with a weight-average MW (Mw) of 1900 g/mol was purchased from Aldrich and was used as received. Tetrahydrofuran (THF) was purchased from Beijing Chemicals Co. and was purified with the standard method. To obtain the blend samples of PEO113-b-PVK77 and PAA, the two polymers were dissolved in a common solvent of THF under mechanical stirring. After becoming transparent, the solutions were stirred for more than 12 h at room temperature. The homogeneous solutions were cast on Teflon sheets and were dried under ambient conditions for 12 h. In order to reach the equilibrium state as much as possible, the samples were subjected to THF-vapor annealing for 2 weeks using the method.
described in literatures.\textsuperscript{33,34} Afterward, the samples were placed in vacuum at room temperature for 3 days to remove the residual THF.

To obtain the samples of PEO\textsubscript{113}-b-PVK\textsubscript{77}/PAA with different compositions, we weighted the two polymers carefully before solution blending. The \(w_{PAA}\) was ranged from 6\% to 95\%. The relationship between \(w_{PAA}\) and the molar ratio of repeating unit of PAA to that of PEO (\([\text{AA}]_\text{PAA}]/[\text{EO}]\) is \([\text{AA}]_\text{PAA}/[\text{EO}] = (w_{PAA}/72)/(1 - w_{PAA}) \times 25\%/44\)], where 72 and 44 are the molar masses of the repeating units of PAA and PEO, respectively, and 25\% is the weight fraction of PEO block in the pure PEO\textsubscript{113}-b-PVK\textsubscript{77}. The volume fraction of PVK in PEO can be estimated as \(\phi_{PVK} \approx [(1-w_{PAA}) \times 75\%/[\text{PVK}]/(w_{PAA}/[\text{PAA}] + (1 - w_{PAA}) \times 25\%/[\text{PEO}] + (1 - w_{PAA}) \times 75\%/[\text{PVK}])\]. The values of densities of amorphous PVK (\(\rho_{PVK}\)) and PEO (\(\rho_{PEO}\)) are taken from literatures,\textsuperscript{35,36} which are 1.184 and 1.211 g/cm\(^3\), respectively. Using a floating technique, the density of the PAA (\(\rho_{PAA}\)) used was measured to be 1.215 g/cm\(^3\).

**Equipment and Experiments.** The thermal behaviors of the pure diblock and the PEO\textsubscript{113}-b-PVK\textsubscript{77}/PAA blends were studied using PerkinElmer Pyris I DSC. The temperature and heat flow were calibrated with benzoic acid and indium. The samples were encapsulated in hermetically sealed aluminum pans with a typical weight of \(8\) mg. For the pure diblock, the temperature range of DSC experiments was 0–240 °C. In order to avoid the decomposition of PAA at high temperatures, the blend samples were just heated to 150 °C at a rate of 10 °C/min.

FTIR spectra of the samples were measured on a Bruker VECTOR22 FTIR spectrometer with a spectral resolution of 4 cm\(^{-1}\). To obtain the spectra with an acceptable signal-to-noise ratio, 32 scans were accumulated. The FTIR spectra were obtained by casting THF solutions (1\% w/v) onto KBr pellets followed by THF-vapor annealing for 2 weeks, and then was dried under vacuum environment at room temperature.

Simultaneous measurements of SAXS and wide-angle X-ray scattering (WAXS) of the samples were performed with a high-flux SAXS instrument (SAXSess, Anton Paar) equipped with a Kratky block-collimation system and a 3 kW ceramic tube as the X-ray source (Cu K\textalpha{}). The scattering patterns of both SAXS and WAXS were recorded on an imaging-plate (IP) with a pixel size of 42.3 × 42.3 \(\mu\)m\(^2\) which extended to high-angle range (the range of \(q\) covered by the IP was from 0.06 to 29 nm\(^{-1}\), \(q = 4\pi\sin(\theta)/\lambda\), where \(\lambda\) is the wavelength of 0.1542 nm and \(2\theta\) the scattering angle). The scattering peak positions were calibrated with silicon powder for wide-angle region and silver behenate for small-angle region, respectively. Background subtraction and desmeasuring was performed by using SAXSquant 3.6 software.

The morphologies of the blend samples were studied by TEM (Hitachi 9000) operated at an accelerating voltage of 100 kV. Leica EM UC6 ultramicrotome was used to prepare the microtomed samples. Thin sections of \(~50\) nm were collected on TEM copper grids, followed by staining in RuO\(_4\) vapor for approximately 15 min. We observed that the PVK domains were preferentially stained, which might be due to that the unsaturated carbazole groups can be stained more than the PEO/PAA complex. We also examined the blend samples after water etching under TEM. To prepare the etched samples, a small piece of a blend after THF-vapor annealing and drying was put into deionized water. After gently stirred for \(~1\) h, the small piece was completely broken into very small particles, and most of the PAA chains were dissolved in water. The particle suspensions were deposited onto TEM grids that were precoated with a thin carbon film of carbon, followed by drying freely at ambient conditions and then in vacuum for days. Parts of the etched samples on the copper grids were stained by uranyl acetate aqueous solution (1.0 wt \%) before drying. The macroscopic morphologies of the blends were examined by phase contrast optical microscopy (Olympus BX51) using the samples cast from THF solution (1\% w/v) on glass sheets and also annealed by THF vapor.

### RESULTS

#### Overall Phase Behavior of PEO\textsubscript{113}-b-PVK\textsubscript{77}/PAA Blends. Phase behavior of the pure PEO\textsubscript{113}-b-PVK\textsubscript{77}, was first examined by means of SAXS/WAXS and DSC experiments. For the freshly dried samples obtained by precipitation or casting from solutions, no X-ray scattering peak appeared in the small-angle region, while two halos centered at 20 of 8.1° and 20° were observed in the high-angle region. This evidenced that the samples were completely disordered on both nanometer and subnanometer scale. Glass transition of the pure diblock sample was rather broad, of which the beginning and ending temperatures were \(~90\) and \(~160\) °C, respectively. In comparison with the homo-PVK with a glass transition temperature \(T_g\) of \(~220\) °C,\textsuperscript{37} PEO\textsubscript{113}-b-PVK\textsubscript{77} possesses a much lower \(T_g\) implying that the PEO and PVK block were at least partially miscible in bulk state. We found that after stored in vacuum for a few weeks the PEO blocks could crystallize partially. Taking the equilibrium heat of fusion (\(\Delta H_f\)) of 7.89 kJ/mol for the low MW PEO as the reference,\textsuperscript{37} the crystallinity of PEO block was estimated to be \(\sim\)38\%. The high-angle diffractions of stored samples could be detected by SAXS/WAXS experiment at room temperature, which appeared at 19.0° and 23.1°, respectively, corresponding to the monoclinic structure of PEO.\textsuperscript{38} The melting temperature of the PEO crystallites was \(~46\) °C, significantly lower than that of homo-PEO with a similar MW. It was noted that the scattering intensity just monotonically decayed in the small-angle region. Therefore, even though the PEO blocks could form crystallites within the sample, the crystallization did not induce clearly microphase separation of the diblock. We concluded that the PEO and PVK block with relatively low MW are largely miscible in bulk state.

According to Zhou and Shi, for a \(af/1\) blend with a miscible \(af/1\) diblock, a large difference between the \(a/C\) and \(b/C\) will drive the blend to be microphase separated. Considering that PAA and PEO can form interchain hydrogen bonding and no specific interaction will exist between PVK and PAA, adding PAA into the diblock should be able to induce the microphase separation of PEO\textsubscript{113}-b-PVK\textsubscript{77}/PAA. A series of PEO\textsubscript{113}-b-PVK\textsubscript{77}/PAA samples were prepared by solution blending. We examined the blend films using phase contrast optical microscopy. For all the PAA compositions, typical morphology of microphase separation was not observed. Of particular interest is to determine whether the blends can truly exhibit microphase separation, and if that is true, then how the PAA content affects the phase structure.

The interchain hydrogen bonding interaction of PEO/PAA was confirmed by FTIR experiments. The asymmetric stretching vibration band of C=O–C is at 1115 cm\(^{-1}\) (vs) for the pure PEO.\textsuperscript{39} After blending with PAA, this band shifted to a lower wavenumber of 1105 cm\(^{-1}\), which should be caused by the interaction between the ether oxygen and the carboxylic acid groups [see the Supporting Information]. The variation of PAA carbonyl stretching vibration band as a function of PAA content of the blends also reflects the formation of PEO/PAA complex. The FTIR of pure PAA has been carefully studied by Nakashima, et al.\textsuperscript{40} They have identified different forms of carboxylic acid groups such as free COOH (1739 cm\(^{-1}\)), cyclic dimer (1705 cm\(^{-1}\)), intramolecular oligomer (1668, 1628 cm\(^{-1}\)), intermolecular oligomer (1668, 1628 cm\(^{-1}\)) and terminal of oligomer (1714 cm\(^{-1}\)). We used the peak at 720 cm\(^{-1}\) which results from out-of-plane vibration of carbazole ring
to normalize the intensity of the original spectra recorded at different compositions (see the Supporting Information). The normalized spectra of carbonyl stretching band of the blends is shown in Figure 1, wherein the band associated with the PEO/ PAA complex shall be also included. It is observed that the band shape is changed with increasing the PAA content. This indicates that the fractions of different forms of −COOH are changed, which should be related to the occurrence of PEO/ PAA complexation. Note that the band of backbone stretching vibration of carbazole ring at 1596 cm$^{-1}$ can be clearly observed in the normalized spectra (illustrated by the ellipse in Figure 1). However, as shown by the inset of Figure 1, it disappears in the differential spectra obtained by choosing the spectrum of pure PEO113-b-PVK77 as the reference. This implies that the carbazole rings are hardly affected by adding PAA, and thus the interaction between PVK and PAA should be minor. In addition to the shape variation of carbonyl stretching band, the integral intensity of whole band continuously increases with wt$_{\text{PAA}}$ as shown in Figure 2. At below wt$_{\text{PAA}}$ of 40%, the integral intensity increases linearly with a small slope. Afterward, increment of PAA content apparently leads to another linear behavior with an increased slope, and finally the integral intensity increases dramatically at above wt$_{\text{PAA}}$ = 70%. Therefore, three different regions in terms of wt$_{\text{PAA}}$ can be identified, which are associated with the different phase behavior of the blends (see the following discussion).

The thermal behaviors of the blends were examined using DSC. We found that addition of a small amount of PAA could greatly suppress the PEO crystallization.\cite{41,42} When wt$_{\text{PAA}}$ exceeded 15%, no melting peak was detected upon DSC heating scan after the samples were stored at room temperature for a long time. On the other hand, for wt$_{\text{PAA}}$ > 30%, a new glass transition below 90 °C rather than that of the pure PEO113-b- PVK77 (around 130 °C) could be clearly observed (see the Supporting Information). As shown in Figure 3, the $T_g$ value gradually increases with increasing the PAA content, approaching to the $T_g$ of the pure PAA at $\sim$92 °C. Considering that the $T_g$ of PEO is around $\sim$67 °C, this glass transition shall be associated with the mixing of PAA and PEO. Assuming that two homopolymers of PAA ($M_w$ of 1900 g/mol) and PEO were mixed, we calculated the $T_g$ of such a mixture based on the Fox equation.

Figure 1. Carbonyl stretching vibration bands of PEO113-b-PVK77/ PAA with various compositions. The spectra were normalized using the peak at 720 cm$^{-1}$ of the out-of-plane vibration of carbazole ring. The interval of the increment of wt$_{\text{PAA}}$ is 10 wt %. The ellipse in the figure indicates the backbone stretching vibration of carbazole ring at 1596 cm$^{-1}$. It disappears in the differential spectra (see the inset of the figure).

Figure 2. Integral intensity of carbonyl stretching band obtained from the differential spectra as a function of PAA content (wt$_{\text{PAA}}$) or the molar ratio of repeating unit of PAA to that of PEO ([AA]:[EO]).

Figure 3. Glass transition temperatures of PEO113-b-PVK77/PAA blends with various PAA contents measured by DSC heating experiment at a rate of 10 °C/min. The red dashed line represents the $T_g$ of the mixture of homopolymers of PEO and PAA ($M_w$ of 1900 g/mol) calculated based on the Fox equation.
homo-PVK. However, to avoid the decomposition of PAA, our DSC experiments of the blends were only run to 150 °C, still far below the $T_g$ of homo-PVK.

The phase morphologies of PEO$_{113}$-b-PVK$_{77}$/PAA blends were investigated by SAXS/WAXS experiments. The WAXS results demonstrated that the blends with $w_{\text{PAA}} < 15\%$ (i.e., $[\text{AA}]/[\text{EO}] < 0.5$) showed weak diffractions of PEO crystallites after the samples were stored at room temperature for a long time, while the blends with higher PAA contents were completely amorphous on the subnanometer scale. This inferred that one PAA chain could interact with several PEO blocks, and consequently hinders the tendency of PEO crystallization. Figure 4a shows the SAXS profiles of PEO$_{113}$-b-PVK$_{77}$/PAA blends with different PAA weight fractions recorded by using SAXSess at room temperature. The intensities of the profiles were normalized using the scattering halo of amorphous PVK block centered at $q = 5.76$ nm$^{-1}$ (i.e., $2\theta = 8.1^\circ$). (b) Long period ($L_p$) corresponding to the scattering peak at $q^*$ as a function of PAA weight fraction.

Phase Morphology Identification. The PAA composition dependence of the phase behavior of PEO$_{113}$-b-PVK$_{77}$/PAA blends is crucial. In general, the SAXS results evidence more directly that the complexation of PAA/PEO can induce the microphase separation of PEO$_{113}$-b-PVK$_{77}$/PAA. Addition of small amount of PAA just causes local density fluctuations, giving the broad scattering on the SAXS profiles, but no ordered morphology exists. For $w_{\text{PAA}} > 70\%$, one may presume that the discrete domains with the core of PVK and the interface of PEO/PAA complex are embedded in the continuous phase of PAA, which can give complex scattering behavior. When $w_{\text{PAA}}$ is ranged from 40 to 70%, the blends render higher-order scatterings which are associated with some ordered microphase-separated structures. Figure 5 shows the enlarged SAXS profiles of these samples. Unfortunately, the higher-order scatterings look diffusive and weak even after the samples were subjected to the THF vapor annealing for a very long time, indicating that the long-range order was just poorly developed. This may be mainly due to the fact that the diblock synthesized by RAFT method using the PEO macromolecular chain transfer agent inevitably contained some residual homo-PVK which was hard to be removed completely by fractionation. Besides, the rigid PVK domain formed after solvent evaporation may lock the phase morphology, preventing the system to relax to the equilibrium state.

Figure 5. Enlarged SAXS profiles of PEO$_{113}$-b-PVK$_{77}$/PAA blends with $w_{\text{PAA}}$ ranged from 40% to 70%. The arrows indicate where the higher-order scatterings should appear for the lamella, cylinder, and cubic phases.

As shown by Figure 4b, the samples with 40% < $w_{\text{PAA}}$ < 70%, i.e., 44% < $f_{\text{PVK}}$ < 22%, possesses a nearly constant $L_p$ of ~23 nm. For the case of PEO-b-PPO-b-PEO (Pluronic P105)/PAA blends studied by Watkins et al.,$^{26}$ it is observed that continuous adding PAA causes the phase morphology changing from lamella to cylinder. The long period of the lamellar phase just increases modestly with increasing the PAA content, which is thought to be mainly caused by that the sample contains some low MW diblock of PEO-b-PPO. Over a wide range of composition, the lamellar and cylindrical phase of P105/PAA possess the $d$-spacings of the first-order scatterings quite close...
to each other. For the blends with a nearly constant \( L_p \) encountered here, the existence of residual homo-PVK may also make the \( L_p \) insensitive to the variation of PAA content. Moreover, careful examination of the SAXS profiles shown in Figure 5 can reveal some different characteristic of higher-order scatterings for the samples with different PAA contents, implying that the phase morphologies may be different. In the following, we intend to determine the phase structure on the basis of a combination of the SAXS and TEM experiments as well as volumetric consideration.

To observe the phase morphologies of the blends under TEM, we prepared the samples using microtomy as well as water-etching method. We found that the blend samples were very brittle at the low temperature of liquid nitrogen. Consequently, the microtomy was quite difficult to perform. Therefore, we further designed an etching method to prepare the TEM sample. The blends was etched by water, which can selectively remove the homo-PAA while does not affect the PVK domain significantly. During water etching, the blend particles would break into small pieces so that the internal morphology of the blend can be observed more clearly. Here, one caution should be reminded: although the PVK is insoluble in water, the PEO blocks tethered on the PVK domain can be swollen by water, which may cause the deformation of the original morphology after PAA was washed out. Nevertheless, we consider that the TEM results of the etched samples prepared in mild conditions can still provide valuable information since PVK domains can be retained to a large extent.

For the sample of \( wt_{PAA} = 41.2\% \), the \( f_{PVK} \) is estimated to be 43.9\%. With this composition, the most possible structure of the blend is lamellar phase, which is fairly suggested by the SAXS profile (see Figure 5). Figure 6a depicts the TEM image of a microtomed sample (\( wt_{PAA} = 41.2\% \)) stained with RuO4, which presents a strip-like pattern with an apparent periodicity of \( \sim 25 \) nm, close to the \( L_p \) of 23 nm measured by SAXS. Considering that the unsaturated carbazole groups may react more with the stain agent, the darker part should be associated with the PVK domains. However, the strip-like pattern looks faint, which implied that the interface between the PVK and PEO/PAA is either diffuse or irregular. Moreover, the dark region is much thicker than the light one, of which the thickness ratio is of \( \sim 2:1 \). If assuming that the sample with \( f_{PVK} \) of 43.9\% forms a regular lamellar structure with flat interfaces, the PVK and PEO/PAA layer should be 10.1 and 12.9 nm thick in terms of their volume fractions, respectively, which is inconsistent with the TEM result. In Figure 6b of a TEM image recorded from a water-etched sample with \( wt_{PAA} = 41.2\% \), the stack of flat-on layers can be seen (indexed by the arrows), which can be taken as an indicative of lamellar structure. However, we also found that the etched sample under TEM could present a morphology that resembles “cylindrical phase”. As shown in Figure 6c, the layer seems to be constructed by coalesced cylinders parallel to each other. In this case, combining the TEM results obtained from the microtomy and etching method, we presume that the layers of the lamellar structure within the sample may be constructed by the parallel
packing of cylinders, the interfaces between PVK and PEO/ PAA domains are somewhat “undulated”.

The imperfect lamellar structure with possibly “undulated” interfaces observed under TEM may account for the weak second-order scattering and the broad peak widths. The formation of this morphology can be related to the solvent from which the sample was cast. As in our experiment, THF was chosen as the common solvent for both of the diblocks and PAA. However, as a proton-acceptor solvent, THF may be preferential for PAA and thus retard the complexation between PAA and PEO. As a result, the PVK block could precipitate out first during the solvent evaporation, leading to “cylindrical micelles” with the core of PVK as the precursor of the final morphology. Figure 6d shows the SAXS profile of the blend sample obtained right after the solution casting. For comparison, the plot of $I_q^2$ vs $q$ of the sample subjected to THF-vapor annealing followed by thoroughly drying in vacuum is also included in Figure 6d, which evidences more the lamellar structure. For the freshly casted sample, the scattering peaks follow a $q$-ratio of $1:3^{1/2}:2$, suggesting the existence of a cylinder structure. After annealing and drying, the sample gives the first order scattering slightly moved to lower $q$, and the second order scattering at $3^{1/2}q^*$ vanishes, indicating the originally hexagonal packing is largely lost. Most likely, the blend tended to relax to a lamellar phase which is more stable at the specific volume fraction of $f_{PVK} = 43.9\%$. However, a lamellar structure with flat interfaces was not achieved. The coalescence of parallel cylinders stopped somewhere, resulting in the “undulated” lamellar structure analogues to the kinetically trapped transition state along the lamellar-cylindrical phase boundary of diblock copolymer melts theoretically discussed by Laradji et al.

Addition of more PAA could result in cylinder phase of the blend system, because of the reduction of $f_{PVK}$. As shown in Figure 5, the sample with $w_{PAA}$ of 48.7% (i.e., $f_{PVK} = 38.5\%$) roughly exhibits the scatterings at a spacing ratios of $1:3^{1/2}:2$. Figure 7 depicts a TEM image of the etched sample with $w_{PAA}$ of 48.7%, wherein the parallel packing of cylinders can be seen. Etching the sample with a prolong time could lead the cylinders to be separated (see Figure 7b). Using uranyl acetate to selectively stain PEO blocks, we find that the cylinder possesses dark periphery. The light core with an average diameter of $\sim 17$ nm of the cylinder shall be composed of PVK blocks. In Figure 7b, the perimeter of some cylinders exhibits some deformation when they were dispersed in water. Assuming that the cylinders pack on a hexagonal lattice, the $L_p$ of 22.4 nm (see Figure 4b) corresponds to the lattice dimension of $a = b = 26$ nm. In this case, the volume fraction occupied by the $\sim 17$ nm-thick cylinder of PVK can be calculated to be 39%, almost identical to the value of $f_{PVK}$ estimated based on the weight fraction and the densities.
Therefore, although the blend lacks well developed long-range order, its hexagonal cylindrical phase can be identified. The ~17 nm diameter of the PVK core is in fact close to the twice of the unperturbed end-to-end distance of the PVK block ($R_0$). Taking the value of 15.9 for the $C_\infty$ of PVK, the $R_0$ of the PVK block with $DP = 77$ is calculated to be ~8.8 nm. Therefore, the conformation of PVK chains along the radial direction on the cylinder is largely unchanged. On the other hand, the unperturbed end-to-end distance of PEO block with $DP = 113$ ($R_{PEO}$) is estimated to be ~6.3 nm, which is significantly smaller than the distance between two adjacent cylindrical domains of PVK. We presume that the PEO blocks are stretched after they form the hydrogen bonding complex with the inserted PAA chains.

We found that the blends entered sphere phases at $w_{PAA} > 50\%$. Figures 8a and 8b present two TEM images of the blend with $w_{PAA}$ of 56.5\% (i.e., $f_{PVK} = 27.4\%$) taken from a microtomed and an etched sample, respectively. In Figure 8a, the close packing of spheres implies a body-centered cubic (BCC) phase with the PVK domain size of ~16 nm, although the cubic phase cannot be unambiguously evidenced by the SAXS result. As shown in Figure 5, the higher-angle scatterings of the cubic phase, which should appear at the positions indexed by the arrows, are largely overlapped. Nevertheless, on the basis of $f_{PVK} = 32.7\%$ and $L_p = 23$ nm (see Figure 4b) for this blend, the diameter of PVK sphere in the BCC structure can be estimated to be 15.6 nm, rather close to that measured from TEM result. For the sample with $w_{PAA}$ of 63.7\% (i.e., $f_{PVK} = 27.4\%$), spheres were also observed under TEM (see the Supporting Information), of which the domain size was almost the same as that with $w_{PAA}$ of 56.5\%. For the blends with $w_{PAA}$ higher than 70\%, the etched samples without stain always showed aggregates of spheres and some individual ones (see the Supporting Information). The spheres with the diameter around 20–23 nm were rather uniform, which should have the core of PVK blocks and the shell containing PEO blocks. As shown in Figure 4b, increasing $w_{PAA}$ results in the increase of $L_p$, indicating the spheres become more and more apart from each other. As the PAA is the majority of blends, a dispersed sphere phase with PAA as the continuous phase was observed.

## DISCUSSION

The experimental results obtained from various techniques demonstrate that addition of PAA into the PEO-$b$-PVK blend can lead to microphase separation of the blend system, and moreover, the phase morphology can be tuned by varying the composition regions can be revealed not only by SAXS but also by FTIR and DSC experiments, which in fact detect different properties of the blends. The coincidence suggests that the microphase separation of the PAA/PEO-$b$-PVK blend is tightly related to the degree of PAA/PEO complexation.

The behavior of carbonyl absorption varying with the PAA content shown in Figure 2 is not fully understood at this moment. Tentatively, we consider that it reflects the change of environment of the COOH groups. At $w_{PAA} < 40\%$, the PAA chains surrounded by the diblocks have abundant opportunity to interact with PEO. However, the COOH groups do not completely interact with the complementary binding sites on PEO, which should be mainly due to the steric hindrance between the polymer chains. A shoulder of absorption peak located at ~1740 cm$^{-1}$ is clearly observed, suggesting the existence of free COOH groups ($\nu$ of 1739 cm$^{-1}$). A stoichiometrical process of PAA/PEO complexation with [AA]$/[EO] = 1$, which is at $w_{PAA} = 29\%$, is not achieved in our blends. In this case, the PAA chains are homogeneously mixed with the PEO blocks, in despite of the existence of PVK blocks. This may account for that the Fox equation can fairly describe the $T_g$ of the blends with low PAA content (i.e., $w_{PAA} < 40\%$).

To obtain the microphase separation throughout the sample, more binding sites of every PEO block are required to participate in complexation, and thus adding more PAA chains is necessary. At $w_{PAA} = 41.2\%$, a lamellar phase can be obtained. At this composition the value of [AA]$/[EO]$ is 1.72, namely, the [AA] is significantly excess. The cyclic dimer and other types of COOH groups can exist within the PAA/PEO domains, resulting in increased carbonyl absorption at ~1700 cm$^{-1}$. After $w_{PAA} = 70\%$, the hydrogen bonding interaction between PAA and PEO should be saturated to a large extent. The exceeded PAA chains forms a continuous phase, giving the FTIR spectrum more similar to that of pure PAA. Note that for the blends with $40\% < w_{PAA} < 70\%$, the $T_g$ values present a positive deviation relative to that calculated by the Fox equation, but are still significantly lower than the $T_g$ of the pure PAA. This also suggests that the complexation between PAA and PEO does not result in the ideal ladder structure which should have a $T_g$ higher than the homo-PAA. Namely, the PEO/PAA complex in our blends is loose one.

It is important to note that the stoichiometrical complexation of PAA/PEO does not occur in our blend system. After the PAA/PEO complexation induces the microphase separation, the PAA/PEO complex domain still allows the invasion of new PAA chains, which will naturally lead to the increase of interfacial area per PEO block (equivalently, per PVK block). In our previous study of vesicle formation in a blend solution of PAA and poly(ethylene oxide)-b-polybutadiene (PEO-$b$-PB), we observed that in a selective solvent of PB the vesicular membrane was composed of a core of PAA/PEO complex and the shell of PB. In a wide composition range, the vesicle size can be controlled by adjusting the ratio of PAA to PEO-$b$-PB, and the interfacial area per block ($s$, in nm$^2$) is found to be linearly proportional to [AA]/[EO]. Using the data ref 49, we obtain

$$ s \approx 2.12 + 1.72([AA]/[EO]) $$

Assuming that the PAA/PEO complex core in the vesicular membrane is nearly solvent free and thus eq 1 can be applied to analyze the blend system studied here, the $s$ for the blend with $w_{PAA} = 56.5\%$ (i.e., [AA]/[EO] = 3.18) is estimated to be 7.6 nm$^2$. On the basis of the size of PVK sphere with a diameter of ~16 nm and $R_{PVK}$ of 1.184 g/cm$^3$, the aggregation number of PVK blocks in the sphere is ~103, and therefore, the $s$ is ~7.8 nm$^2$, in good agreement with that calculated using eq 1.

It is interesting to infer that when a lamellar phase with flat interface is formed how the value of [AA]/[EO] will be. Assuming the PVK blocks possess the length of ~8.8 nm (i.e., the value of $R_{PVK}$), the $s$ of the flat interface should be ~2.4 nm$^2$, corresponding to a [AA]/[EO] of 0.16 estimated based on eq 1. As mentioned above, at such a low [AA]/[EO], the PAA/
PEO complexation is far from sufficient to induce the microphase separation with ordered structures. When the PVK and PEO/PAA complex are gradually separated into two domains, insertion of more PAA chains into the complex domain tends to enlarge the interfacial area per PEO block. For the blend with a lamellar phase at \( \varphi_{\text{PEO}} = 41.2\% \) (i.e., [AA]:[EO] = 1.72), eq 1 gives the \( s \) value of \( \sim 5.0\) nm\(^2\). Assuming that the PVK blocks which are semirigid resist to be deformed too much, one way to meet the demand of increasing interfacial area is to allow the interface to be convex. If it is the case, the sample with an “undulated” lamellar structure could be understood.

Zhou and Shi’s theoretical calculation gives the prediction on the transition boundary between different ordered morphologies for \( \alpha/\beta/C \) blends, wherein the three pairs of \( \alpha/\beta, \alpha/C, \) and \( \beta/C \) are miscible but \( \alpha/C \) and \( \beta/C \) pair interactions are sufficiently different.\(^{23}\) Also they predict the reverse morphology where the majority of diblock forms the continuous phase of ordered structures and the minority homopolymer enters the core. For our blend system, the phase evolution at \( \varphi_{\text{PAA}} > 40\% \) is in accordance with the theoretical result. However, at low PAA contents, the inverse “micelle” with PAA/PEO complex as the core cannot be observed. A reasonable explanation is that the interaction of PAA/PEO, which is a local event, may have a \([\text{AA}]:[\text{EO}]\) dependence. When only a small part of the PEO binding sites are used, the PAA chains added do not have an enough strong power to completely extract the PEO blocks which originally mix with the PVK blocks. In this case, only a sort of density fluctuation exists, giving the broad scattering peak as shown in Figure 4a. Once the sufficient amount of PEO/PAA complexation is reached at a critical \([\text{AA}]:[\text{EO}]\) (here, the value should be around 1.7), the PEO/PAA and PVK become truly immiscible, and then the PEO/\(113^-\)/PVK77/PAA system undergoes microphase separation with ordered structures.

**CONCLUSIONS**

In summary, we have investigated the phase behavior of a new \( \alpha/\beta/C \) type polymer blend of PEO\(113^-\)/PVK77/PAA (\( M_w = 1900 \) g/mol) using various characterization techniques. The results indicate that while the PEO and PVK blocks are miscible, blending of the diblock with homo-PAA is an effective way to induce the microphase separation. The added PAA has 2-fold effects: one is to selectively interact with PEO block via interchain hydrogen bonding, forming PEO/PAA complex which is effectively immiscible with the PVK block; the other is to change the volume fraction and thus the spontaneous curvature of interfaces of the ordered structures. The experimental results imply that the strength of interchain hydrogen bonding interaction between PAA and PEO is composition dependent. Only when sufficient amount of PAA is blended with PEO\(113^-\)/PVK77, the interchain complexation of PEO/PAA can extract the PEO blocks, leading to the formation of pure PVK domains in the blend. While addition of small amount of PAA just causes density fluctuation of the blend system, microphase separation with different ordered structures can be achieved at \( \varphi_{\text{PAA}} > 40\% \), although the long-range order is not well developed. Combining the SAXS with TEM results, we consider that with increasing the PAA content, the blend system can exhibit the lamellar, cylindrical, cubic, and dispersed sphere phase. Physically, the strong attractive interaction and entropy of mixing causes the homo-PAA to insert and swell the PEO blocks, curving the interface toward the PVK domains. On the other hand, the semirigid PVK block with \( DP = 77 \) is not deformed too much during microphase separation. As a result, the PVK domain size of \( \sim 17 \) nm measured from the TEM images of etched sample with cylinder and sphere phase is almost identical to the twice of the unperturbed end-to-end distance of the PVK block. We expect that the hydrogen bond assisted microphase separation of PEO-b-PVK/PAA blend can also present nanostructured pattern in its thin films,\(^{41}\) of which may be useful in the design of PVK-based electro-optical devices. The experiment of the thin film of PEO-b-PVK/PAA blend is currently undergoing in our lab, and the results will be reported in the near future.

**ASSOCIATED CONTENT**

Supporting Information

FTIR, DSC results of the PEO\(113^-\)/PVK77/PAA blends, and TEM images of the water-etched sample with \( \varphi_{\text{PAA}} > 60\% \). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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