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Complexation and eutectic crystallization in poly(2-vinyl pyridine)-*block*-poly(ε-caprolactone) and pentadecylphenol mixtures

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ABSTRACT

Crystallization behavior via hydrogen bonding interaction in amphiphilic block copolymer/surfactant mixtures consisting of poly(2-vinyl pyridine)-*block*-poly(ε-caprolactone) (P2VP–PCL) and 3-pentadecylphenol (PDP) were investigated by differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. The P2VP–PCL/PDP mixtures exhibit eutectic crystallization behavior; the eutectic composition is approximately at 70 wt.% PDP. Scanning probe microscopy (SPM) observation revealed the microphase structure in the P2VP–PCL/PDP mixtures and the unique eutectic morphology at the eutectic composition, which was further confirmed by small angle X-ray scattering (SAXS) results. To our knowledge, this is the first example of eutectic crystallization observed in amphiphilic block copolymer/surfactant systems. The FTIR study proved that there are competitive hydrogen bonding interactions between P2VP block/PDP and PCL block/PDP pairs in the P2VP–PCL/PDP mixtures. On the basis of the SPM results and FTIR study, a model describing the microstructure of the P2VP–PCL/PDP eutectic mixtures is proposed. The amorphous P2VP blocks are expelled from the ordered eutectic lamellae formed by the crystalline PCL blocks and PDP, which deviates remarkably from the existing structural model proposed by other authors for poly(vinyl pyridine)/PDP and poly(styrene-*block*-4-vinyl pyridine)/PDP mixtures.

1. Introduction

Hydrogen bonding is one of the significant and highly directional non-covalent interactions which plays important roles in many functions and properties of substance, especially in biological fields [1–5]. In the field of polymer processing, hydrogen bonding is employed to improve the miscibility between different polymers [6–10]. Hydrogen bonds can also act as the bridge in forming complexes or supramolecular structures composed of different kinds of molecules, such as the interesting comb-like "block copolymer" obtained in the mixtures of poly(vinyl pyridine) and amphiphilic surfactant 3-pentadecylphenol (PDP) [11–17].

In recent years, the complexes of surfactant and polymer have received extensive concerns due to their ordered structures in various scales and the ability in morphology control compared with the traditional copolymers. In the system of poly(4-vinyl pyridine) (P4VP) and PDP, it was found that the mesomorphic structure could be formed in the mixtures of non-mesogenic substance once the condition was tailored well [18]. The similar phenomenon could also been observed in the mixtures of polyacids and matching surfactants with the ionic bonding [19–21]. Though the supramolecular structure based on the hydrogen bonds is under thermodynamic equilibrium and the hydrogen bond is not as firm as the covalent bonds, it is still enough for the complexes to exhibit many characteristics similar to the real block copolymers, such as the lamellar, cylindric and other microphase separated morphologies.

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Furthermore, in the P4VP/PDP mixtures, it was found that the tails of PDP molecules combined with P4VP can cocrystallize with other non-associated PDP molecules and the obtained crystallite is with a lower melting point compared with the normal PDP crystallites [13]. In mixtures of surfactant and amphiphilic block copolymer containing a poly(vinyl pyridine) block, more interesting structures can be explored. The change in the order–disorder transitions or conversely and in interaction parameters with the addition of salt or surfactant to block copolymers have been studied by Mayes and Cruz [22], Bates et al. [23], and Russell et al. [24]. The poly(styrene-*block*-4-vinyl pyridine) (PS-P4VP)/PDP and the PS-P4VP/methane sulfonic acid/PDP mixtures have received great attention recently [25–33]. It has been well documented that additional structure periodicity in different length scales from the original one can be introduced into the mixture system by microphase separation. It was proved that with the variation in PDP content in PS-P4VP/PDP mixtures, spherical, hexagonal and lamellar structure could be observed. This offered the possibility to adjust the self-organized structure in multiscales through ordered–disordered transitions. A good example is controlling the electrical conduction of materials by manipulating microstructures through temperature-dependent transitions [25].

In these mixture systems, the hydrophobic PS block is amorphous and its property is rather different from any other components in the mixtures, i.e., the hydrophilic P4VP block and PDP. Its effects on the mixture property, especially on the microphase structure and morphology in the nanometer scales, have been deliberately investigated. As it is known, the miscibility between the PS blocks and the P4VP block chains or the surfactant molecule PDP is poor. The miscibility is an important factor to determine the final microphase morphology, apart from the block length and the volume fraction of the components.

The eutectic crystallization behavior in PCL/PDP binary blends has been investigated in our previous study [34]. Here we report the results of an investigation into amphiphilic block copolymer/surfactant mixtures of poly(2-vinyl pyridine)-*block*-poly(ε-caprolactone) (P2VP–PCL) and PDP. The carbonyl groups of PCL have the possibility to form hydrogen bonds with the phenol hydroxyls of PDP, as shown in Fig. 1. Due to the repulsive non-polar PDP side groups linked to the block copolymer by the hydrogen bonding force, comb-shaped supramolecular structure can be obtained. The coexistence of three kinds of hydrogen bonds, i.e., in the P2VP/PDP, PCL/PDP and PDP/PDP pairs, will bring about the competition of the PDP distribution among PCL and P2VP microdomains, and even in PDP crystallite where the self-association of PDP molecules exists. In the present P2VP–PCL/PDP block copolymer/surfactant system, the hydrogen bonding interactions are examined. Moreover, PCL is a crystalline polymer; the structure and morphology of this block copolymer/surfactant system can be enriched by incorporating a second self-assembling mechanism, i.e., block crystallization. In particular, unusual eutectic crystallization behavior was found in this mixture system and studied in detail. To our knowledge, this is the first example of eutectic crystallization observed in amphiphilic block copolymer/surfactant systems.

2. Experimental section

2.1. Materials and preparation of mixture solutions

Poly(2-vinylpyridine)-*block*-poly(ε-caprolactone) (P2VP–PCL) diblock copolymer was a product of Polymer Scouce, Inc. The weight-averaged molecular weights M_w of P2VP and PCL blocks were 2.09×10^4 and 2.61×10^4, respectively. The M_w/M_n of the copolymer was 1.11. Poly(ε-caprolactone) (PCL) with $M_w = 1.4 \times 10^4$ and 3-pentadecylphenol (PDP) (technical grade) were products of Aldrich Chemical Company, Inc. Chloroform (Aldrich) was the analytical grade and was used as received. To prepare the mixture solution, PDP was first dissolved in chloroform till a clear solution was obtained. Then an appropriate amount of P2VP–PCL diblock copolymer was added into the solution and stirred at room temperature to obtain transparent solution. The concentration of the solution was kept below 1 wt.% (w/v) to avoid the contraction of P2VP–PCL copolymer and PDP molecules in the

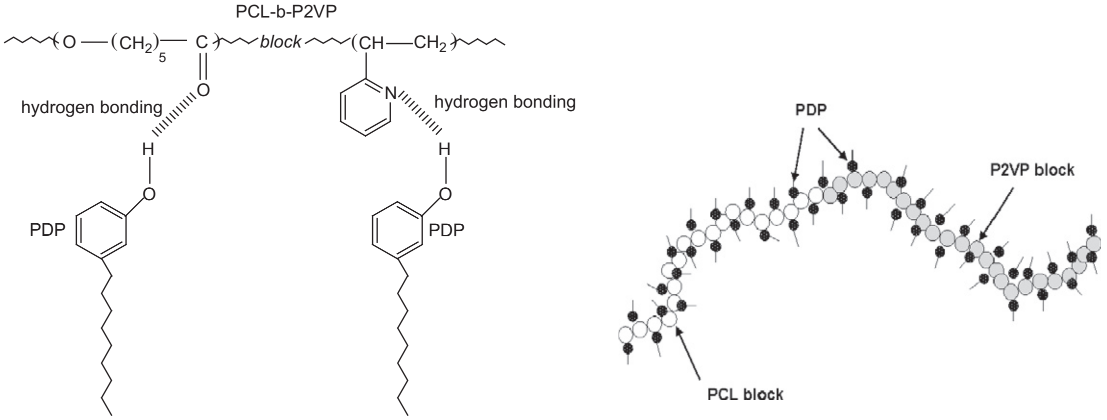

Fig. 1. Schematic representation of the proposed interactions in P2VP–PCL/PDP mixtures.

solution. The PCL/PDP mixture solutions were prepared in the same way. To obtain the solid samples, the solvent was removed completely by vacuum evaporation.

2.2. Differential scanning calorimetry

A Perkin–Elmer Diamond DSC was used to investigate the thermal properties of the samples. All the samples were first melted at 100 °C for 5 min to remove the thermal history and then cooled to −60 °C at a rate of 5 °C/min. The samples were subsequently heated to 100 °C again with a heating rate of 5 °C/min (second scan). The samples for DSC measurements were cast from the mixture solutions at room temperature and then dried for 72 h under vacuum to remove the residual solvent. The weight of sample for DSC experiment was in the range of 5–10 mg.

2.3. Scanning probe microscopy

SPM images were recorded under ambient conditions using a scanning probe microscope (DME type DS 45-40, Denmark), operating in the tapping mode. Si cantilever tips (TESP) with a resonance frequency of approximately 300 kHz and a spring constant of 40 N m^{-1} were used, and the tips were calibrated before measurements. The height and phase images were recorded simultaneously during the scan. The specimens for observation were obtained by solution casting on glass substrates. All the specimens were placed in vacuum at room temperature for 24 h to remove the residual solvent. For SPM experiments, the specimens were first melt at 80 °C for 5 min, and then isothermally crystallized at 25 °C for 72 h.

2.4. Infrared spectroscopy

Infrared measurements were performed on a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector. The experiments were carried out by using an average of 32 scans and a resolution of 4 cm^{-1}. To prepare the specimens for infrared measurement, the mixture solution was cast onto a potassium bromide (KBr) window. The concentration of the sample solution was constant for all the sample compositions. After the solvent evaporated at room temperature, the specimens were dried under vacuum for 24 h. Before measuring, the specimens were heated to 80 °C under the protection of nitrogen atmosphere, held for 5 min to remove the thermal history, and then isothermally crystallized at 25 °C for 72 h.

2.5. Small-angle X-ray scattering

The SAXS measurements were conducted with a Bruker NanoSTAR instrument using a HR-PHK high resolution pinhole chamber with CuKα1 radiation source (λ = 0.154 nm). The scattering position was calibrated using the rattail standard. Two-dimensional diffraction patterns collected at room temperature were subtracted from background scattering, corrected for response characteristics, and converted into a one-dimensional format (intensity vs. q) by azimuthal averaging of the data ($q = (4\pi/\lambda)\sin(\theta/2)$ is the scattering wavevector). For SAXS experiments, the samples were first melt at 80 °C for 5 min, and then isothermally crystallized at 25 °C for 72 h.

3. Results and discussion

3.1. Crystallization behavior of P2VP–PCL/PDP mixtures

The comb-like self-assembly systems involving poly(vinyl pyridine)/PDP and P4VP–PS/PDP mixtures have received considerable attentions over the last decade due to the flexible control of the supramolecular structure. In the present study, the introduction of crystalline PCL blocks into such a self-assembly system brings about new characteristics, especially coupling and competition during crystallization.

The crystallization ability of the PCL blocks in P2VP–PCL diblock copolymer was investigated firstly. As shown in Fig. 2, crystalline spherulites of P2VP–PCL copolymer were clearly observed with polarized optical microscope. DSC results in Fig. 3 display that the melting point and crystallization temperature of the copolymer are 60.4 and 36 °C, respectively. These values are very close to those of the PCL homopolymer with the approximate molecular weights [35,36]. The crystallinity of the PCL blocks in the copolymer was calculated to be 50% from the DSC heating scan, according to the weight fraction of PCL blocks in the copolymer, and the enthalpy of fusion for 100% crystalline PCL, which is 139.5 J/g according to Pitt et al. [37]. So it can be concluded that the PCL block in the P2VP–PCL copolymer has considerable crystallization ability. Thus there are two crystalline components in the P2VP–PCL/PDP mixture; one is the PCL block and the other is surfactant PDP.

The crystallization behavior of a similar diblock copolymer, poly(4-vinyl pyridine)-*block*-poly(ε-caprolactone) was previously studied by Sun et al. [38]. It was proven that the crystallization of PCL was confined in the nanoscale due to the strong microphase separation. Moreover, the nucleation type was also changed under some extremely confined condition. The P2VP–PCL block copolymer

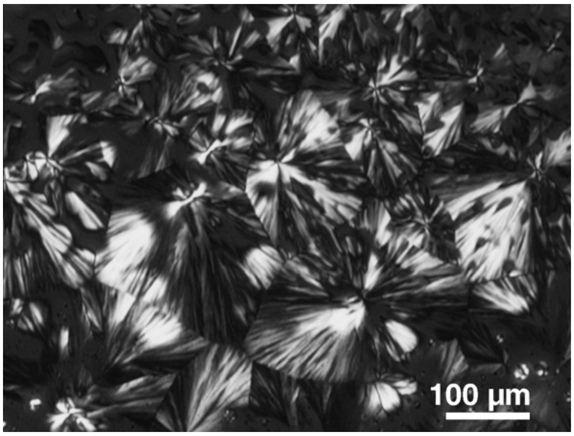

Fig. 2. Semicrystalline morphology of the pure P2VP–PCL block copolymer under polarizing optical microscope. The sample was isothermally crystallized at 36 °C for 4 h and the image was taken at this temperature.

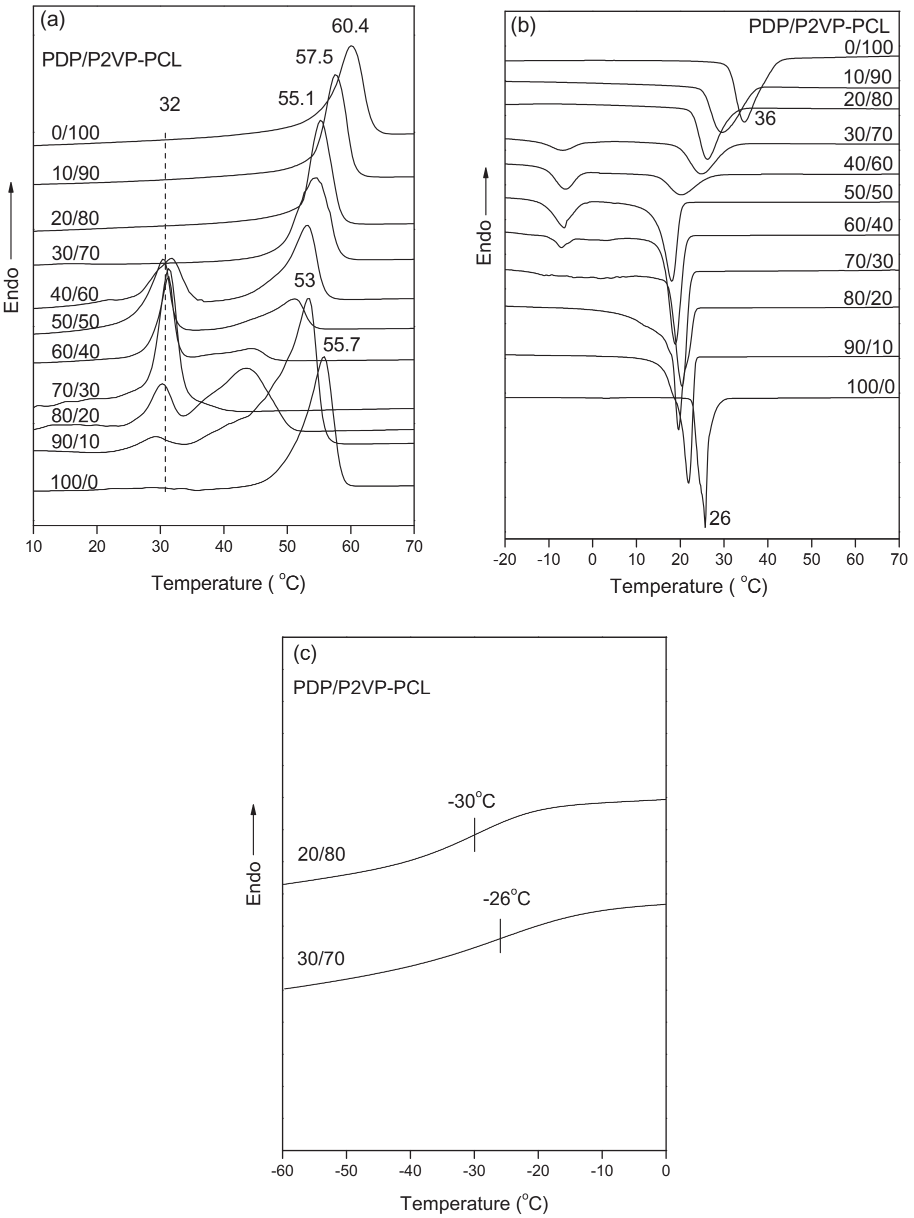

Fig. 3. DSC curves of P2VP–PCL/PDP mixtures: (a) second scans at 5 °C/min; (b) cooling scans at −5 °C/min after melt at 100 °C for 5 min; and (c) DSC curves of second scans at 5 °C/min in the glass transition region of 20/80 and 30/70 P2VP–PCL/PDP mixtures.

in this study has a relatively longer block chain both in PCL and P2VP blocks; the confined crystallization characteristics also appears, which will be proved by SPM study presented below.

Melting and crystallization behaviors of the P2VP–PCL/PDP mixtures were studied by DSC. The results are shown in Figs. 3 and 4. The melting points of crystalline PCL blocks and PDP were detected to be 60.4 and 55.7 °C, respectively. The melting points of the mixtures significantly depend on the composition. At most compositions, two melting points were detected, which implies that there was more than one kind of phase transformation in the second scans (Fig. 4a).

Moreover, it is noticed that in the samples within certain composition range (50–80 wt.% PDP), some melting peaks remain around 32 °C and are not changed with the composition. This phenomenon exhibits the characteristic of a eutectic mixture system.

Eutectic crystallization is a common phenomenon for growing composites in metallic and inorganic materials [39]. While in polymeric systems, eutectic crystallization is not as usual as in the other material fields. The eutectic crystallization behavior was found in polyethylene and high melting diluents systems [40], poly(L-lactide acid)/parahydroxybenzoic acid systems [41]. Recently, the eutectic crystallization behavior in biomacromolecules and

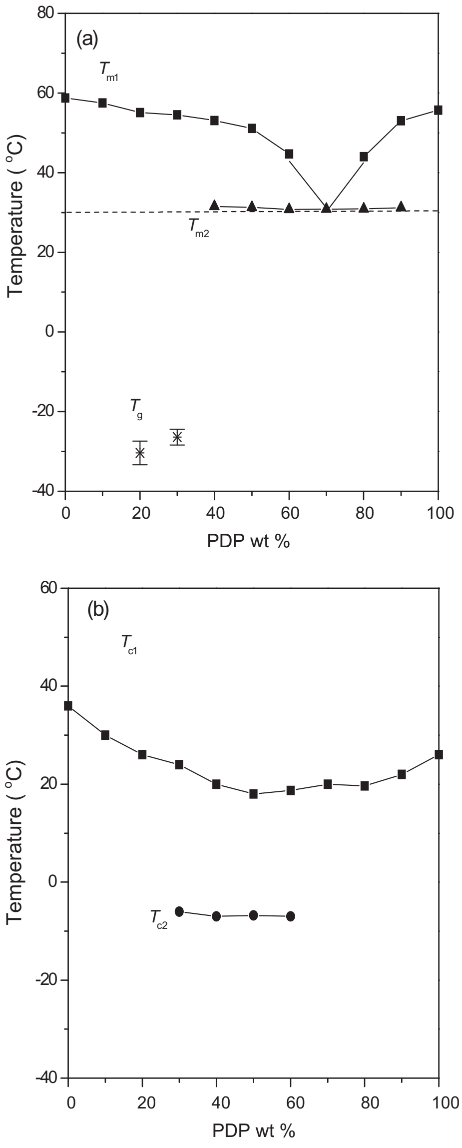

Fig. 4. Thermal transitions of P2VP–PCL/PDP mixtures from DSC curves of (a) the second scans and (b) the cooling scans.

low molecular weight chemical medicine systems has received increasing concern for the application in the drugs controlled release field [42–44].

Evidently, the melting point around 32 °C, i.e., T_{m2}, for the P2VP–PCL/PDP mixtures come from the eutectic structure, which is a homogeneous mixture of PCL block crystals and PDP crystals. The melting points at the higher temperatures, T_{m1}, belong to either the crystallites of pure PCL block or the PDP crystals depending on the concentration. The eutectic composition is approximately at 70 wt.% PDP from Fig. 4a.

Glass transition temperature, T_g, was detected in some mixtures under the experimental temperature conditions. The T_g values of −30 and −26 °C presented in Figs. 3c and 4a are for the mixture with 20 and 30 wt.% PDP, respectively. It was documented in literature that the T_g value of PCL is −60 °C [45,46] while that of P2VP block in the diblock copolymer was detected to be 105 °C by DSC. Therefore the glass transition detected in the P2VP–PCL/PDP mixtures with 20 and 30 wt.% PDP can be ascribed to the microphase composed of mainly PCL blocks.

To further understand the eutectic crystallization behavior of P2VP–PCL/PDP mixture system, the PCL/PDP mixtures within the entire composition range were investigated by DSC. Fig. 5 shows DSC curves of the second scan of the PCL/PDP mixtures at a heating rate of 5 °C/min. The eutectic crystallization behavior is clearly seen. The eutectic composition is 60 wt.% PDP, slightly deviated from to that of the P2VP–PCL/PDP system, which is 70 wt.% PDP. However, if we take the PCL content in the copolymer into

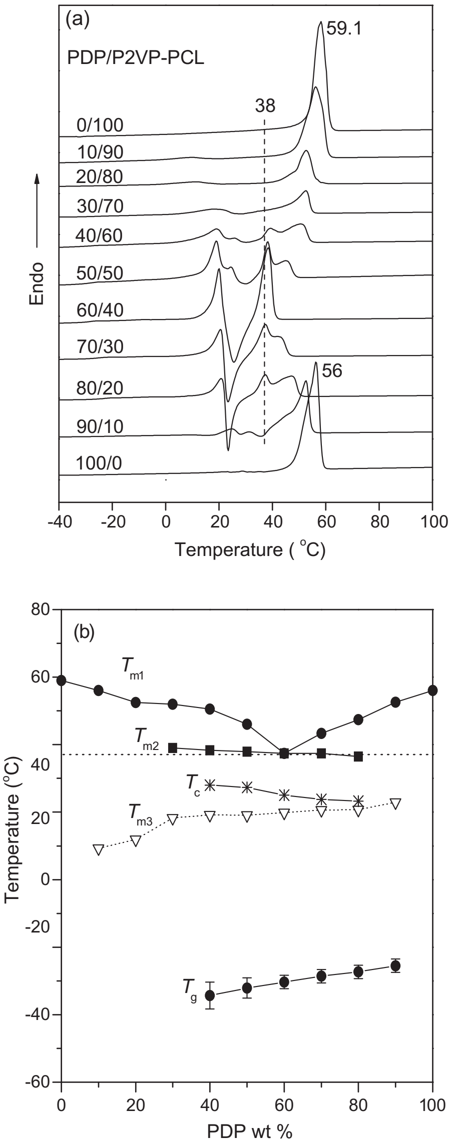

Fig. 5. Thermal properties of PCL/PDP mixtures. (a) DSC curves of the second scan at 5 °C/min; (b) thermal transition temperatures.

account, an even more profound difference in the eutectic composition between these two mixture systems can be discerned. This implies that considerable amount of PDP was dissolved in the microphase composed of P2VP blocks.

The plain PCL exhibits a melting temperature of 59.1 °C which is slightly lower than that of the pure P2VP–PCL block copolymer (60.4 °C). However, the eutectic temperature is 38 °C for PCL/PDP system, which is approximately 6 °C higher than that in P2VP–PCL/PDP system. The lower eutectic temperature in the P2VP–PCL/PDP can be attributed to the defects in the P2VP–PCL/PDP eutectic mixture due to the interference of P2VP blocks. In our previous study [34], we have observed the eutectic crystallization behavior in mixtures of PCL homopolymer and PDP and found that morphology at eutectic composition is different from the other compositions.

Meanwhile, glass transitions were detected to be in the range of −40 to −20 °C for the PCL/PDP mixture with 40–90 wt.% PDP. The T_g values increase with the PDP content. From this observation, it is evident that the interaction between PCL chain and PDP is the main reason for the increase of the T_g of PCL. This explanation also responds for the T_g increase in the P2VP–PCL/PDP mixtures as mentioned above.

From the apparent evidence of hydrogen bonding between PCL and PDP, the comb-shape self-assembly structures can be supposed in the PCL/PDP mixtures, as that in the poly(vinyl pyridine)/PDP system. However, the formation of comb-shape self-assembly may be affected by the strong crystallization ability in the PCL/PDP system.

The SPM phase images of P2VP–PCL/PDP mixtures with 40 and 70 wt.% PDP are shown in Fig. 6a and b, respectively. Microphase separation is still the main characteristic in these mixtures. Particularly, typical in-plane meandering lamellar morphology stands out in the mixture with 70 wt.% PDP, i.e., the eutectic composition (Fig. 6b). The microdomains take the orientation parallel to the mixture film surface. Besides, classic island topography is also displayed in the image. The period of lamellae is calculated to be approximately 58 nm. Taking the DSC results and the finding of eutectic behavior into account, it can be assumed that the bright areas in the phase image are of eutectic mixture whereas the dark areas correspond to the non-crystalline regions, mainly composed of amorphous P2VP. This speculation differs from the reported structure in the P4VP–PS/PDP systems, where P4VP and PDP self-assemble cooperatively into the ordered comb-shape structures while the PS blocks form the disordered microdomains.

The SAXS profiles of annealed P2VP–PCL/PDP samples were taken at room temperature in order to confirm the morphology obtained in SPM analysis and are shown in

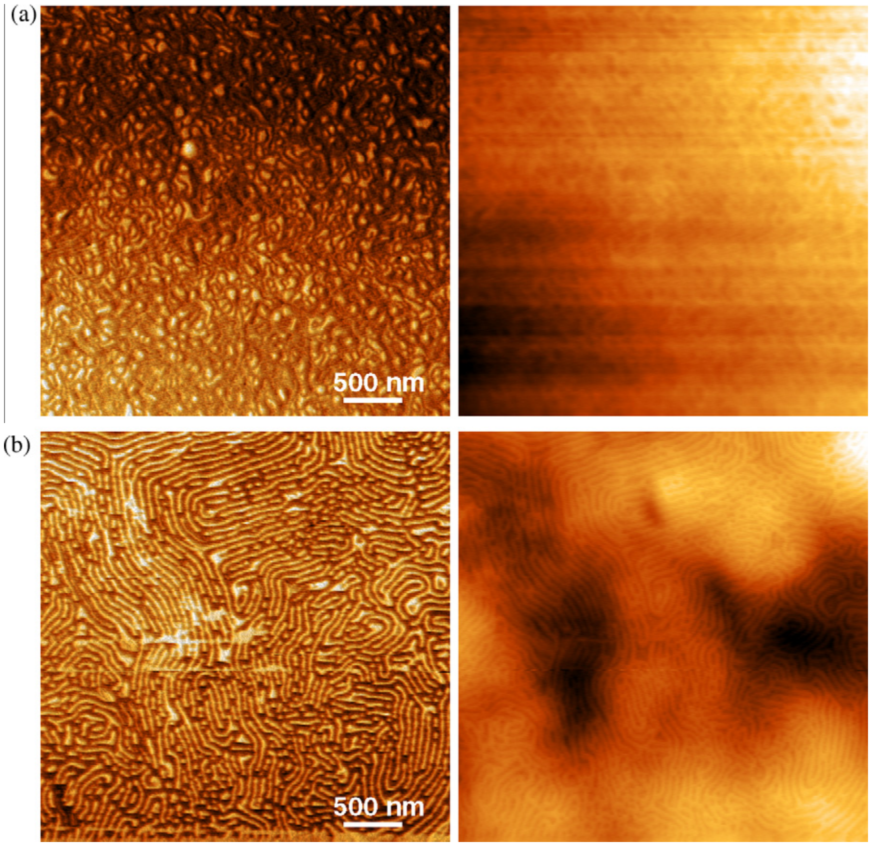

Fig. 6. SPM images of (a) P2VP–PCL/PDP mixture film with 40 wt.% PDP, and (b) P2VP–PCL/PDP mixture film with 70 wt.% PDP; left is the phase image and right the height image (the height scale in 245 nm).

Fig. 7. The SAXS profiles were shifted vertically to avoid overlap. For pure P2VP–PCL block copolymer, the first order scattering peak corresponds to a spacing of 18.2 nm which is the average distance between the PCL and neighboring P2VP microphases [5]. The peak positions in the SAXS profile indicate of hexagonally-packed cylindrical morphology, i.e., $q/q^* = \surd 1{:}\surd 3{:}\surd 4{:}\surd 7\ldots$ (Here, q^* is the wave vector at the maximum intensity of SAXS profiles.) [43,45]. The 40 wt.% PDP mixture shows a broad peak and the broadening of the peak indicates the absence of long range ordered structures. However, the SAXS profile of eutectic mixture (i.e., 70 wt.% PDP) again displays the characteristics of lamellar morphology and the peak positions notably shift to lower q values, indicating an increase of the spacing (54.8 nm). Moreover, the SAXS profile of the eutectic mixture shows another peak at very high q value ($q = 1.75\ \mathrm{nm}^{-1}$), which can be attributed to the PDP crystalline phase alone [13] or P4VP/PDP pair with or without crystallization of the alkyl tails. This arises from the interaction between P4VP and PDP, but at the same time the quantity of this combination is relatively less compared to the PCL/PDP pair.

To further explore the inner structures of the regularly alternating lamellar regions in the P2VP–PVL/PDP mixtures, the interaction behavior in the mixtures with different compositions was investigated by infrared spectroscopy.

3.2. Complexation behavior of P2VP–PCL/PDP mixtures

From the chemical structures of P2VP–PCL and PDP, interactions may form not only between P2VP block and PDP, but also between PCL block and PDP. These mixtures come from the hydrogen bonds between pyridine ring of P2VP blocks and phenol hydroxyl group of PDP and between carbonyl of PCL blocks and phenol hydroxyl group, respectively.

Infrared spectroscopy is a powerful technique in the exploration of molecular interactions. It can give the most direct structural information on the molecular scales, including the association of molecules. The study of hydrogen bonding interaction between poly(vinyl pyridine) and PDP utilizing FTIR has received much concern during the last decade. It is well known that the characteristic infrared absorption changes related with this intermolecular interaction are the bands at 1590, 993, and 625 cm^{-1} for P2VP and 1597, 993, and 627 cm^{-1} for P4VP [47,48].

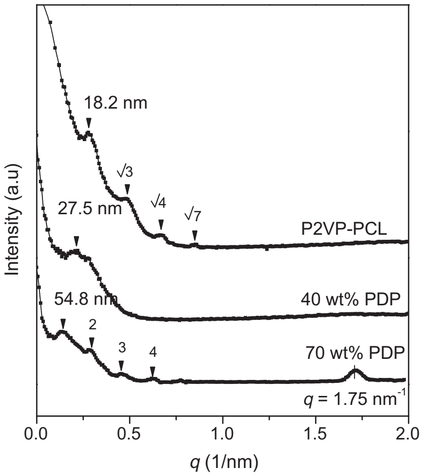

Fig. 7. SAXS profiles of P2VP–PCL/PDP mixtures.

The infrared spectra of P2VP–PCL/PDP mixtures are shown in Fig. 8. In the mixtures with 40–80 wt.% PDP, new bands at 1597 and 1006 cm^{-1} appear which can be attributed to the stretching vibration of pyridines in the bonded state. The corresponding original bands at 1590 and 993 cm^{-1} related to the stretching vibration of pyridines in the non-bonded state impair or disappear (Fig. 8b and c) due to the changed chemical environment. Therefore the evidence of hydrogen bonding between P2VP and PDP is obvious. It is also noticed that the composition of the mixture plays an important role on the intensity ratio of the new and original bands. This indicates different degree of hydrogen bonding in different mixtures.

Besides the association of P2VP blocks and PDP, the bonding of carbonyl group in the PCL blocks can also be discerned from infrared spectra, especially in the range of 1780–1680 cm^{-1}, as shown in Fig. 8a. The bonded carbonyl groups often bring about new absorption at a lower wavenumber than that of carbonyl in crystalline (1724 cm^{-1}) and amorphous states (1737 cm^{-1}) [49]. The new band due to hydrogen bonding of the PCL blocks and PDP arises at the wavenumber of 1715 cm^{-1}. It is found that the intensity of the new band grows with the increase of PDP amount in the mixtures, which means that the more PDP in the mixtures, the more bonded carbonyl groups of PCL blocks. He et al. [50] reported the inter-associated hydrogen bonds of PCL/4,4′-thiodiphenol mixtures and found the composition and temperature both affected the fraction of hydrogen bonds in the system.

Therefore, the interactions in both P2VP/PDP and PCL/PDP pairs in the P2VP–PCL/PDP mixtures are proven undoubtedly, which means the possibility of comb-shape self-assembly in both P2VP/PDP and PCL/PDP pairs. The eutectic forming binary system consisting of poly(ethylene oxide) (PEO) and *p*-hydroxybenzaldehyde (PHB) was previously investigated by Zhu et al. [49]. They found that at the eutectic composition, the hydrogen bonding association of PHB with PEO reached its maximum and a homogeneous morphology of the blends was observed, respectively. Hence it can be suggested that in P2VP–PCL/PDP eutectic mixture the hydrogen bonding interaction between PCL and PDP is the most predominant. This thus results in the lamellar morphology with a homogeneous PDP/PCL phase and a separated amorphous phase composed of P2VP blocks and PDP molecules as revealed in AFM and SAXS experiments.

3.3. Microstructures in P2VP–PCL/PDP mixtures

Based on the above results, a model describing the microstructures in the P2VP–PCL/PDP mixtures can be proposed, as shown in Fig. 9. For the pure P2VP–PCL block copolymer, microphase separation results in the microdomains where the crystallization of PCL is restricted within

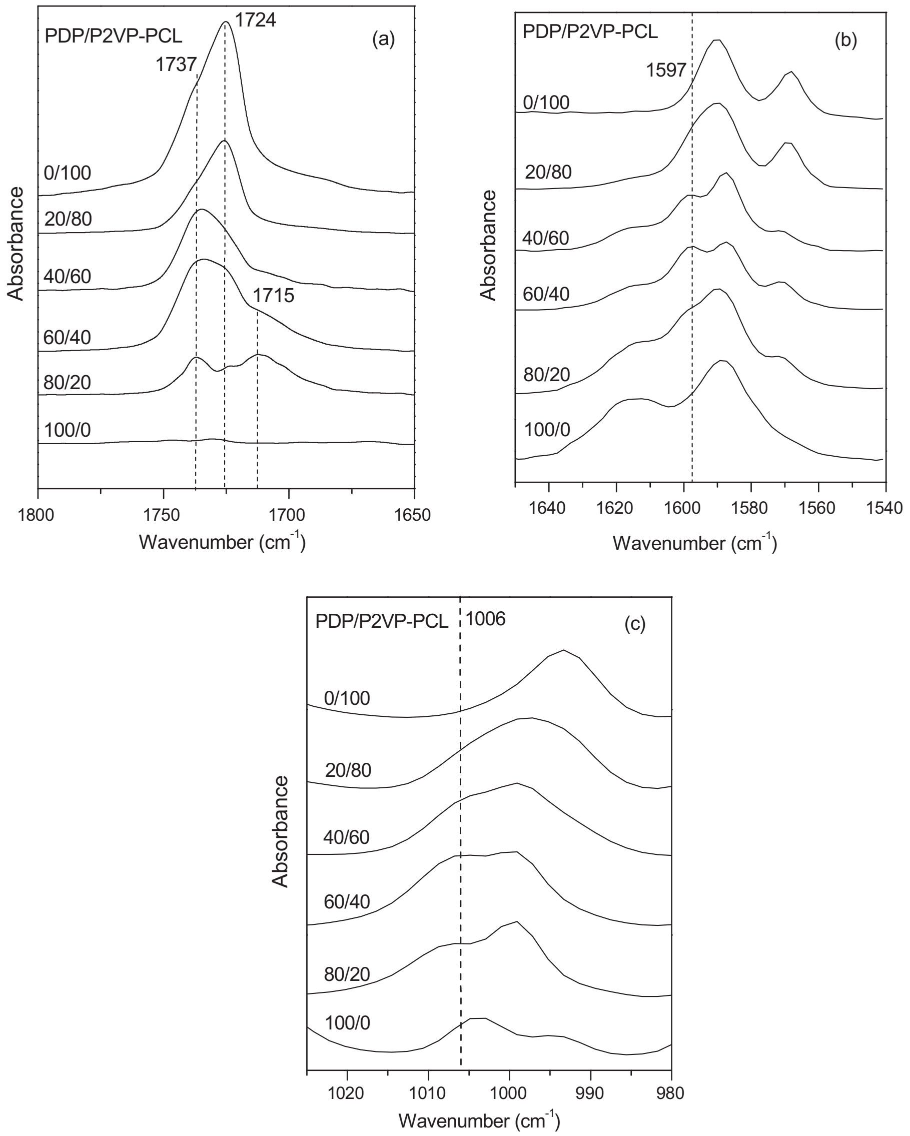

Fig. 8. Infrared spectra of P2VP–PCL/PDP mixtures in the region of (a) 1800–1650 cm^{-1}, (b) 1650–1540 cm^{-1}, and (c)1025–980 cm^{-1}.

the hard confined environment. The hard confinement environment originates from the high glass transition temperature of P2VP blocks, which was detected to be 105 °C. The microstructure is schematically illustrated in Fig. 9a.

The introduction of PDP molecules changes the crystallization environment totally, especially for the mixture with a large amount of PDP. It can be predicted that in the molten state at 80 °C, the P2VP–PCL copolymer are dissolved in the PDP "solvent". The high degree of hydrogen bonding in both P2VP/PDP and PCL/PDP pairs detected by FTIR is indicative of the miscibility. During the quenching and annealing, new crystalline microdomains emerge.

As to the mixture with 70 wt.% PDP, which is the eutectic composition, the P2VP–PCL/PDP mixture is mainly composed of two kinds of microdomains after the annealing, as illustrated in Fig. 9b. The alternating lamellae consists the eutectic structure comprising crystalline PCL blocks and PDP crystals and the lamellae region mainly composed of amorphous P2VP blocks and PDP molecules.

Another block copolymer and low molar mass substance mixture system with eutectic behavior was documented by De Rose et al. [51]. They proposed a structure development process during the directional eutectic solidification. Upon epitaxy of polystyrene-*block*-polyethylene (PS–PE) block copolymer on the benzoic acid (BA) crystals, two-dimensional periodic thin films were obtained. In this system, BA acts as the substrate for the epitaxy of PE since the eutectic temperature is higher than the melting point of the PE blocks. Contrarily, in the present P2VP–PCL/PDP system, the eutectic temperature is lower than the melting points of both the PCL blocks and PDP. Therefore, we propose here a different model to describe the microstructure of the P2VP–PCL/PDP eutectic mixture.

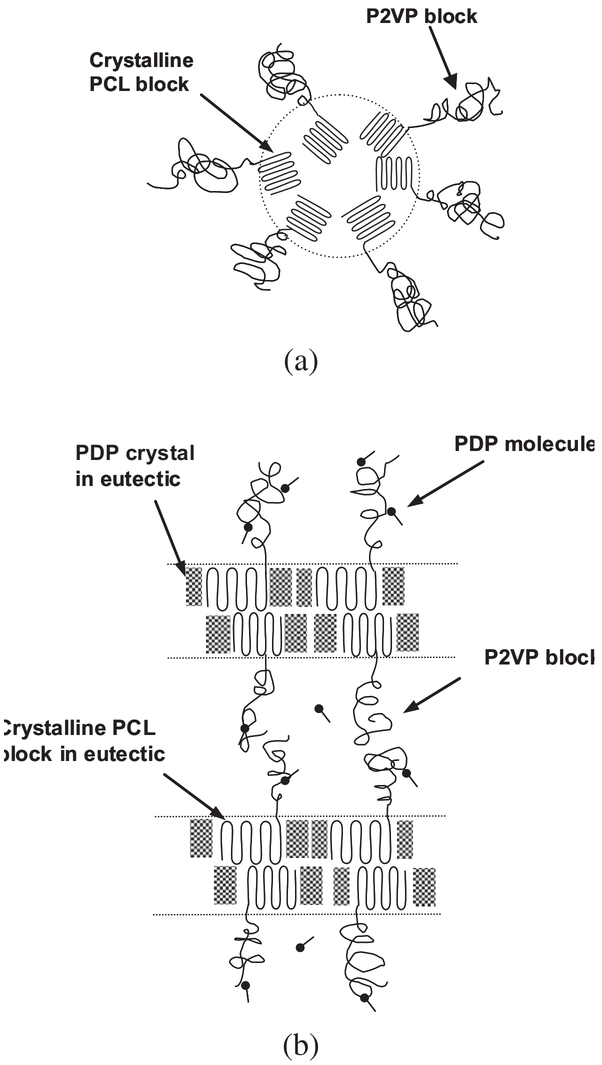

Fig. 9. Schematic representation of the microstructures: (a) crystalline P2VP–PCL block copolymer; (b) P2VP–PCL/PDP eutectic mixture with 70 wt.% PDP.

4. Conclusions

The eutectic crystallization behavior was found in an amphiphilic block copolymer/surfactant mixture system for the first time. The eutectic temperature of the P2VP–PCL/PDP system is 32 °C and the eutectic composition is with 70 wt.% PDP content. The mixture at the eutectic composition exhibits unique microphase separated morphology. The eutectic composition forms lamellar morphology with crystalline microdomains and amorphous regions. The crystalline region consists of PCL blocks and PDP crystals and the amorphous region composed of P2VP blocks and PDP molecules located between them. The results of infrared spectra of the mixture samples reveal the competition of hydrogen bonding among the P2VP/PDP, PCL/PDP and PDP/PDP pairs. Based on the experimental results, a model describing the microstructures is proposed, which is different from the existing models for the mixtures containing PDP and copolymer with poly(vinyl pyridine) blocks.

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