



Solvent annealing assisted self-assembly of hydrogen-bonded interpolymer complexes of AB block copolymer/C homopolymer in thin film

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ARTICLE INFO

Article history:

Received 10 May 2010

Received in revised form

23 July 2010

Accepted 22 August 2010

Available online 16 September 2010

Keywords:

Block copolymer/homopolymer

Self-assembly

Solvent annealing

ABSTRACT

A simple process of solvent annealing has been shown to produce ordered self-assembly structures of poly(styrene)-block-poly(4-vinylpyridine) (PS-*b*-P4VP)/poly(4,4'-oxydiphenylene-pyromellitic acid) (POAA) block copolymer/homopolymer blends in thin film, where POAA chains selectively interact with P4VP blocks by strong interpolymer hydrogen-bonding. By simply exposing the thin film to benzene/NMP (0.97/0.03, in volume) vapor mixture, ordered microphase-separated structures with PS spherical microdomains distributed within P4VP/POAA complexes matrix were obtained. The formation of the microphase-separated structures could be attributed to the substantial mobility of PS blocks and P4VP/POAA complexes and enhanced repulsion between them under the benzene/NMP mixture vapor. When the volume ratio of benzene to NMP increased to 0.98/0.02, the increasing benzene in the mixture vapor induced the adhesive collision of spherical microphase-separated structures to form long "pearl necklaces". With increasing volume ratio of benzene to NMP to 0.99/0.01, an ordered "pearl necklace" array oriented parallel to the film surface formed. The self-assembly structures were studied by FTIR spectroscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM). Finally, possible mechanism of self-assembly and formation of microphase morphology was proposed.

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1. Introduction

In recent years, there has been growing interest in the study of blends of diblock copolymers mixed with homopolymers because it provides fascinating self-assembly behavior to be used as functional nanostructures [1–9]. Especially recently, most of the studies focused on the blends of A-*b*-B/C diblock copolymer/homopolymer, where secondary interactions such as hydrogen-bonding, coordination bonding, ionic interactions are introduced. The presence of interassociated secondary interactions in the blends is very important since it enhances miscibility of the components, and as the result, gives various well-defined periodic self-assembly structures. For example, Lu et al. studied the self-assembly structures of blending of the immiscible poly(ϵ -caprolactone)-block-poly(4-vinyl pyridine) (PCL-*b*-P4VP) diblock copolymer with octa-phenol polyhedral oligomeric silsesquioxane (OP-POSS), and showed that the PCL-*b*-P4VP/OP-POSS blends with different compositions exhibited different microphase-separated structures through the effects of the competitive hydrogen-bonding between

PCL/OP-POSS and P4VP/OP-POSS [10]. Guo et al. studied the selective hydrogen-bonding in poly(ϵ -caprolactone)-block-poly(2-vinylpyridine) (PCL-*b*-P2VP) with poly(4-vinylphenol) (PVPh). The competitive hydrogen-bonding between PVPh/P2VP pair and PVPh/PCL pair resulted in the formation of composition-dependent nanostructures in the complexes [11]. Similarly, Chang et al. investigated the specific interactions, miscibility and self-assembly morphology mediated by hydrogen-bonding interactions, of the blending of poly(ϵ -caprolactone)-block-poly(vinyl phenol) (PCL-*b*-PVPh)/poly(vinyl pyrrolidone) (PVP) [12]. More recently, Matsushita et al. have studied the phase behavior of a poly(styrene-*b*-2-vinylpyridine) block copolymer (SP)/poly(4-hydroxystyrene) (H) blends where the strong selective hydrogen-bonding between H homopolymer and P block induced various nanophase separated structures in a wide composition of the blends, and have also systematically investigated the effect of homopolymer molecular weight on the self-assembled structure of the blends [13,14].

To the best of our knowledge, most of the self-assembly structures of diblock copolymer/homopolymer blends reported previously were achieved via thermal treatment at high temperature for a long time, which is necessary for the thermodynamic equilibrium of the blends. However, thermal treatment is not applicable to some system, especially to the blends of diblock copolymer with

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a homopolymer which will be cured once treated at high temperature. It is well-known that solvent annealing as an effective way to control the microdomain orientation and long-range ordering in block copolymer thin films, has been extensively studied over the past few years [15–19]. The route is simple and could be performed without any thermal treatment. In this work, we have extend solvent treatment to the self-assembly of PS-*b*-P4VP/POAA blends in thin films, where POAA is immiscible with PS blocks but interacts selectively with P4VP blocks via strong interpolymer hydrogen-bonding. During solvent annealing in benzene/NMP mixture vapor, self-assembly structures of PS-*b*-P4VP/POAA thin films were achieved. Furthermore, the self-assembly nanostructures could be adjusted by changing the volume ratio of benzene to NMP in the solvent vapor mixture. Based on the experimental results, possible mechanisms of self-assembly and formation of microphase morphology were proposed.

2. Experiment section

2.1. Materials

PS-*b*-P4VP block copolymer (M_n PS: P4VP = 11800: 15000 g/mol and polydispersity of 1.04) was purchased from Polymer Source Inc., and used as received. POAA homopolymer with a M_w (POAA)_{SLS} of 4.5×10^4 g/mol, was prepared according to our previous report [20]. Benzene and N-Methyl-2-pyrrolidone (NMP) were analytical chemical reagents and used as received.

2.2. Preparation of PS-*b*-P4VP/POAA thin films

The block copolymer PS-*b*-P4VP and POAA homopolymer was first dissolved in NMP respectively, to make polymer solution with a concentration of 5 wt.%. The NMP solution containing 5 wt.% polymer mixtures was stirred for more than 24 h at room temperature. PS-*b*-P4VP/POAA blends in thin films, with a thickness of ~100 nm, were prepared on a silicon wafer by spin-coating at 2000 rpm for 4 min, followed by drying under vacuum at room temperature to remove residual NMP. Table 1 summarizes the composition of pure PS-*b*-P4VP block copolymer and its blends with POAA homopolymer. The blends thin films were solvent annealed in the saturated mixture vapor of benzene (vapor pressure at 80 °C: 101.3 kPa) and NMP (vapor pressure at 80 °C: 1.33 kPa) at 80 °C. Detailed experiments were shown as follows: the thin films were placed in a totally air-tight vessel with 50 ml volume along with one small vial which contained benzene and NMP, with a volume ratio of benzene to NMP ranging from 1/4 to 4/1; the environment outside the vessel was maintained at 80 °C; after solvent annealing for 24 h, the films were removed from the vessel quickly and air-dried at room temperature. The composition of benzene/NMP vapor mixture could be calculating by Raoult' Law (1) and Dalton' Law (2),

$$P_B = P_B^* \cdot x_B \quad (1)$$

$$y_B = \frac{P_B}{P} = \frac{P_B^* \cdot x_B}{P_N^* + (P_B^* - P_N^*) \cdot x_B} \quad (2)$$

where P , P_B is total vapor pressure and benzene vapor pressure in the benzene/NMP vapor mixture; P_B^* , P_N^* is vapor pressure of pure benzene and NMP; x_B , y_B is mole fraction of benzene in solution and vapor, respectively. According to the Raoult' Law (1) and Dalton' Law (2), various compositions of benzene/NMP vapor mixture were examined from benzene volume fraction of 0.95–0.997.

2.3. Characterization

The KBr disk method was adopted to determine the FTIR characteristics of the PS-*b*-P4VP/POAA complexes. The FTIR spectrum was measured using a Bruker IFS 66 V/S FTIR spectrometer. The NMP solution containing the sample was cast onto a KBr disk, and solvent was allowed to evaporate slowly at room temperature. The disks were dried under vacuum in an oven before taking the measurements. The spectra were recorded at the average of 32 scans in the standard wavenumber range of 400–4000 cm^{-1} at a resolution of 1 cm^{-1} . AFM studies were operated at a Nanoscope IIIa multimode atomic force microscope (AFM, Digital Instruments) at the tapping mode. Films for TEM were prepared on silicon substrates having a thick layer of silicon oxide. These films were floated onto the surface of a 5 wt.% HF solution, transferred to a water bath, and then picked up by a Cu grid. Iodine was employed as staining agent to selectively contrast POAA chains and P4VP blocks. The samples were placed in vapors of iodine crystals for 2 h at 35 °C. A JEM 2010 transmission electron microscope operating at an accelerating voltage of 200 kV was used to examine the morphology.

3. Results and discussion

FTIR characterization has been used to investigate the specific interactions in the PS-*b*-P4VP/POAA complexes. Fig. 1 summarizes the possible hydrogen-bonding interactions between POAA homopolymer and PS-*b*-P4VP block copolymer. The carbonyl region ranging from 1800 to 1575 cm^{-1} in the IR spectra of PS-*b*-P4VP/POAA blends is presented in Fig. 2a. The spectrum of pure POAA shows two sharp peaks at 1663 cm^{-1} and 1716 cm^{-1} , corresponding to carbonyl stretching of amide group and carboxylic acid unit, respectively. In the PS-*b*-P4VP/POAA blends, as the concentration of PS-*b*-P4VP increases, both the two peaks shift to higher wavenumbers. The shift could be attributed to the hydrogen-bonding

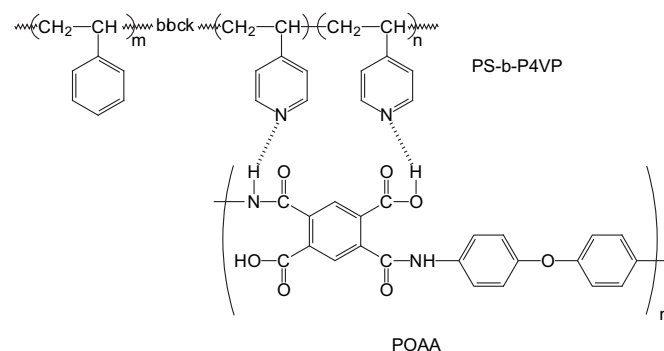


Fig. 1. Schematic representation of possible interactions between POAA homopolymer and PS-*b*-P4VP block copolymer.

Table 1

Composition and possible phase structure of the PS-*b*-P4VP block copolymer and its blends with POAA homopolymer with POAA wt.% of 50%.

polymer	volume fraction		possible self-assembly structure ^a
	Φ_{PS}	$\Phi_{P4VP/POAA}$	
PS- <i>b</i> -P4VP	0.44	0.56	Lamellae
PS- <i>b</i> -P4VP/POAA	0.22	0.78	Spheres or cylinders

^a Possible thermodynamically stable self-assembly structures predicated from relative volume fraction of PS blocks and P4VP/POAA complexes according to the self-consistent mean field theory [21].

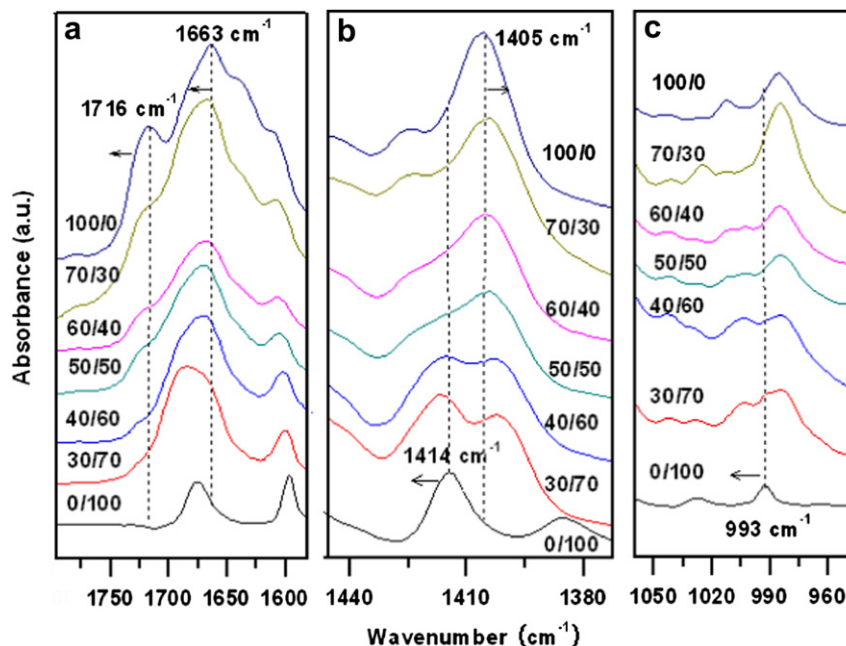


Fig. 2. FTIR spectra displaying the (a) carbonyl stretching, (b) carbon-nitrogen stretching, and (c) distortion vibration of the pyridine ring, of the POAA/PS-b-P4VP complexes with different weight ratio of POAA: PS-b-P4VP.

interaction of secondary amine group of amide and hydroxyl group of carboxylic acid unite with pyridine nitrogen atom of P4VP blocks [22]. With respect to pyridine ring of P4VP blocks, the characteristic adsorption bands at 1414 cm^{-1} and 993 cm^{-1} , corresponding to carbon-nitrogen stretching and distortion vibration of the pyridine ring, are susceptible to hydrogen-bonding interactions. Upon complexation with POAA chains, as shown in Fig. 2b and (c), the peaks at 1414 cm^{-1} and 993 cm^{-1} , are expected to shift to higher wavenumbers, 1417 cm^{-1} and 1004 cm^{-1} , respectively [23]. Moreover, in the FTIR (Fig. 2b), the carbon-nitrogen stretching band of amide group in POAA at 1405 cm^{-1} moves to a lower band at 1401 cm^{-1} , which arises from the increase of C–N bond-length due to the formation of hydrogen-bonding between pyridine nitrogen atom and secondary amine of amide unite. All these results confirm that the hydrogen-bonding interaction between P4VP blocks and POAA chains has taken place in the PS-b-P4VP/POAA blends.

Binary mixtures of block copolymers with homopolymers can form a rich variety of microstructures which are the result of the spontaneous interfacial areas and curvatures that are established at equilibrium. As a result, thermal treatment at high temperature above T_g is necessary to reach equilibrium for the polymer blends. In PS-b-P4VP/POAA system, POAA is immiscible with PS blocks but interacts selectively with P4VP blocks via interpolymer hydrogen-bonding. The incorporation of POAA in the PS-b-P4VP system may increase the interaction parameter difference between PS and P4VP/POAA phases, leading to the strong segregated microphase separation [20]. However, thermal annealing is detrimental to the self-assembly of PS-b-P4VP/POAA blends, because imidization of POAA is induced at high temperature and which will destroy the hydrogen-bonding interaction of P4VP/POAA. Here, solvent annealing at a low temperature is employed to gain self-assembly structures of PS-b-P4VP/POAA, thus avoiding imidization of POAA at high temperature.

Fig. 3a–i shows the AFM and TEM images of the thin films of PS-b-P4VP/POAA blends with a POAA weight percent of 50%, before and after benzene/NMP (0.97/0.03, in volume) annealing at 80°C . Prior to discussion, it should be noted that 80°C was chosen

here for the maximum of vapor pressure of the mixture solvent, which could not induce the imidization of POAA. Before solvent annealing, the height AFM image of the thin film blends indicates a flat surface (Fig. 3a), whereas spherical structure is observed when the thin film was annealed in benzene/NMP mixture vapor for 24 h at 80°C (Fig. 3b). The corresponding AFM phase images as shown in Fig. 3d and e exhibit a homogenous phase for the directly spin-coated thin film and an obvious microphase-separated structure for the solvent annealed thin film. TEM was performed to explore the interior structure of the thin film. After I_2 staining, the POAA and P4VP microdomains are dark, and the PS components appear light. For the directly spin-coated thin film, it is noticed that Fig. 3g represents a homogenous phase, implying no obvious microphase separation occurred. However, when the thin film was annealed in benzene/NMP mixture vapor, the TEM image shown in Fig. 3h presents an ordered structure with spherical PS domains dispersed within P4VP/POAA matrix. The average microdomain diameter and the center-to-center distance are ~ 19 and 32 nm , respectively. The formation of the spherical microphase-separated structure is quite similar to that obtained in blends of block copolymer/homopolymer via thermal annealing in previous reports [10–14], and is consistent with that predicted theoretically as shown in Table 1, indicating the ordered blends thin film is in a thermodynamic equilibrium state after solvent annealing in benzene/NMP at 80°C . In order to compare, the thin film was also treated at 80°C without solvent vapor. As shown in Fig. 3c and f, the thin film becomes more flatter than that before annealing. The TEM image of Fig. 3i displays a characteristic of miscible phase, implying annealing at the same temperature without solvent vapor could not change the phase structure of the as-spun thin film. For the directly spin-coated thin film, a homogenous phase structure formed due to nonselectivity of NMP and high solvent evaporation rate when the thin film was spin-coating from NMP solution. Thermal treatment at a low temperature without solvent annealing could not endow PS blocks and P4VP/POAA complexes with sufficient mobility to reach microphase separation. By contrast, the presence of NMP and benzene vapor could induce

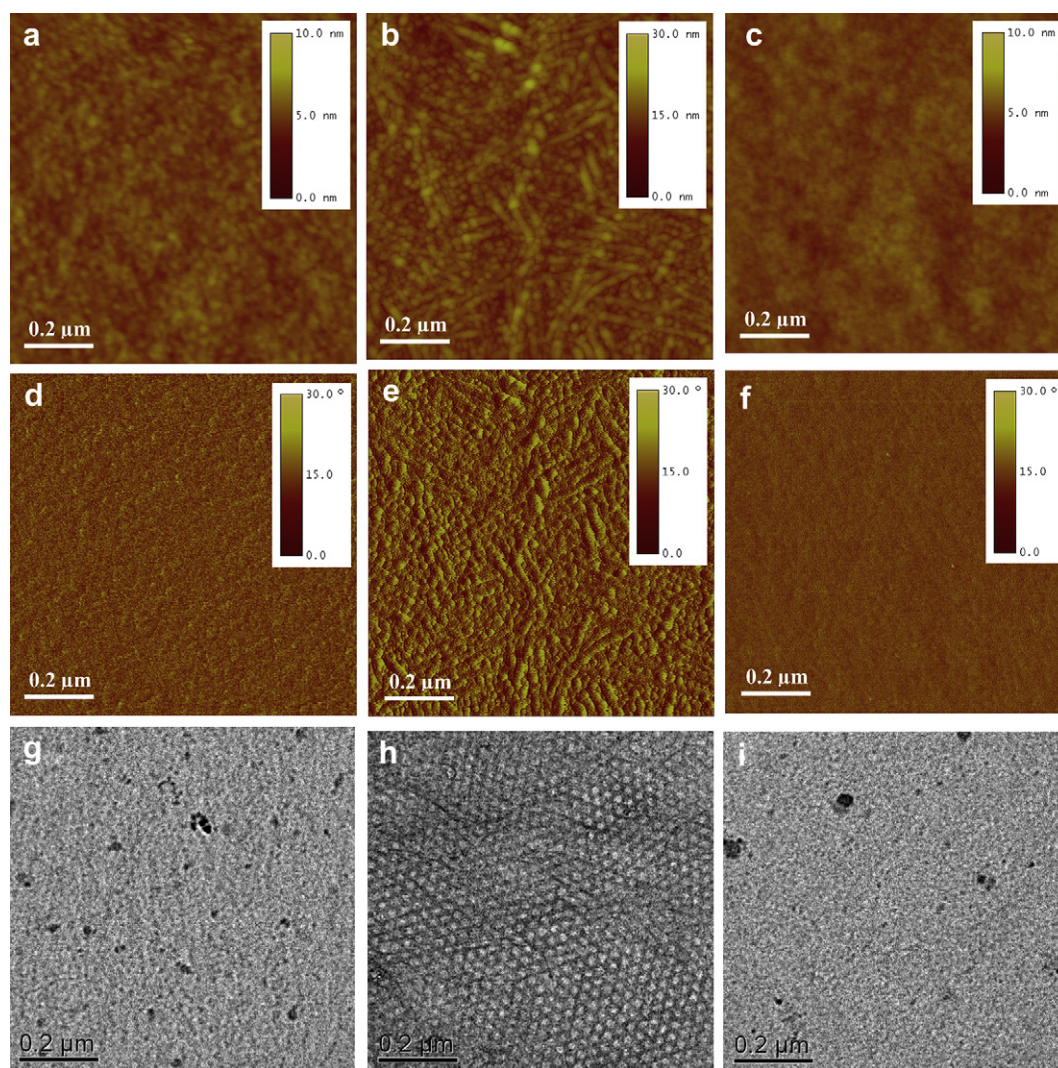


Fig. 3. AFM Height and phase images of PS-b-P4VP/POAA thin film blends (a, d) as-spun, and after annealing (b, e) in benzene/NMP (0.97/0.03, in volume) vapor at 80 °C and (c, f) at 80 °C without solvent vapor. (g), (h), and (i) are corresponding TEM image of (a), (b), and (c), respectively.

microphase separation of the PS-b-P4VP/POAA thin film blends. NMP is a good solvent for both PS-b-P4VP copolymer and POAA homopolymer, under the NMP solvent vapor, PS blocks and P4VP/POAA complexes have quite good mobility, and because of the mobility, the swollen PS and P4VP/POAA complexes repel one another and tend to organize into a well-defined structure. Since benzene is a good solvent only for PS blocks, the presence of benzene could enhance the repulsion between PS blocks and P4VP/POAA complexes, leading to a fast microphase separation in the PS-b-P4VP/POAA thin film blends.

The effect of vapor composition of annealing solvent on the morphology of PS-b-P4VP/POAA thin film blends was studied. Fig. 4a–d show the AFM images of the microphase-separated morphology of PS-b-P4VP/POAA thin film blends with POAA wt.% of 50% after solvent annealing in benzene/NMP vapor with different volume ratios at 80 °C. When the thin film was annealed in benzene/NMP (0.95/0.05, in volume) mixture, spherical structure with diameter of 19 nm was obtained (Fig. 4a). The blends thin film exhibited similar spherical structures after solvent annealing in benzene/NMP (0.97/0.03, in volume) vapor (Fig. 4b). When the thin film was annealed in benzene/NMP (0.98/0.02, in volume) mixture, a mixture of spherical and “pearl necklace” structure formed from

coalescence of spheres is revealed in Fig. 4c. When the PS-b-P4VP/POAA blends thin film was annealed in benzene/NMP (0.99/0.01, in volume) mixture vapor, an exclusive long “pearl necklace” morphology formed and the pearl necklaces were arranged in an ordered array oriented parallel to the film surface (Fig. 4d). TEM was employed to investigate the interior structure of the thin film. Fig. 4e shows the TEM micrograph of the thin film annealed in benzene/NMP (0.95/0.05, in volume) mixture vapor and Fig. 4i displays the image obtained by tilting the specimen by 25° during TEM observation. It can be seen that the thin film presents a disordered microphase separation structure with the PS microdomains dispersed within the P4VP/POAA matrix. Since the image obtained by tilting the specimen by 25° is not significantly different from that shown in Fig. 4e, the TEM observation indicates the thin film exhibits random sphere morphology where the spherical domains are arranged in a liquid-like disorder. For the thin film annealed in benzene/NMP (0.97/0.03, in volume), as shown in Fig. 4f, spherical structures are found to pack in an ordered lattice. From Fig. 4j of the image obtained by tilting the specimen 25°, sphere morphology is also observed but in contrast to Fig. 4f, large area of ordered structure has disappeared and become characterless. Assuming that the spherical domains are arranged in the most

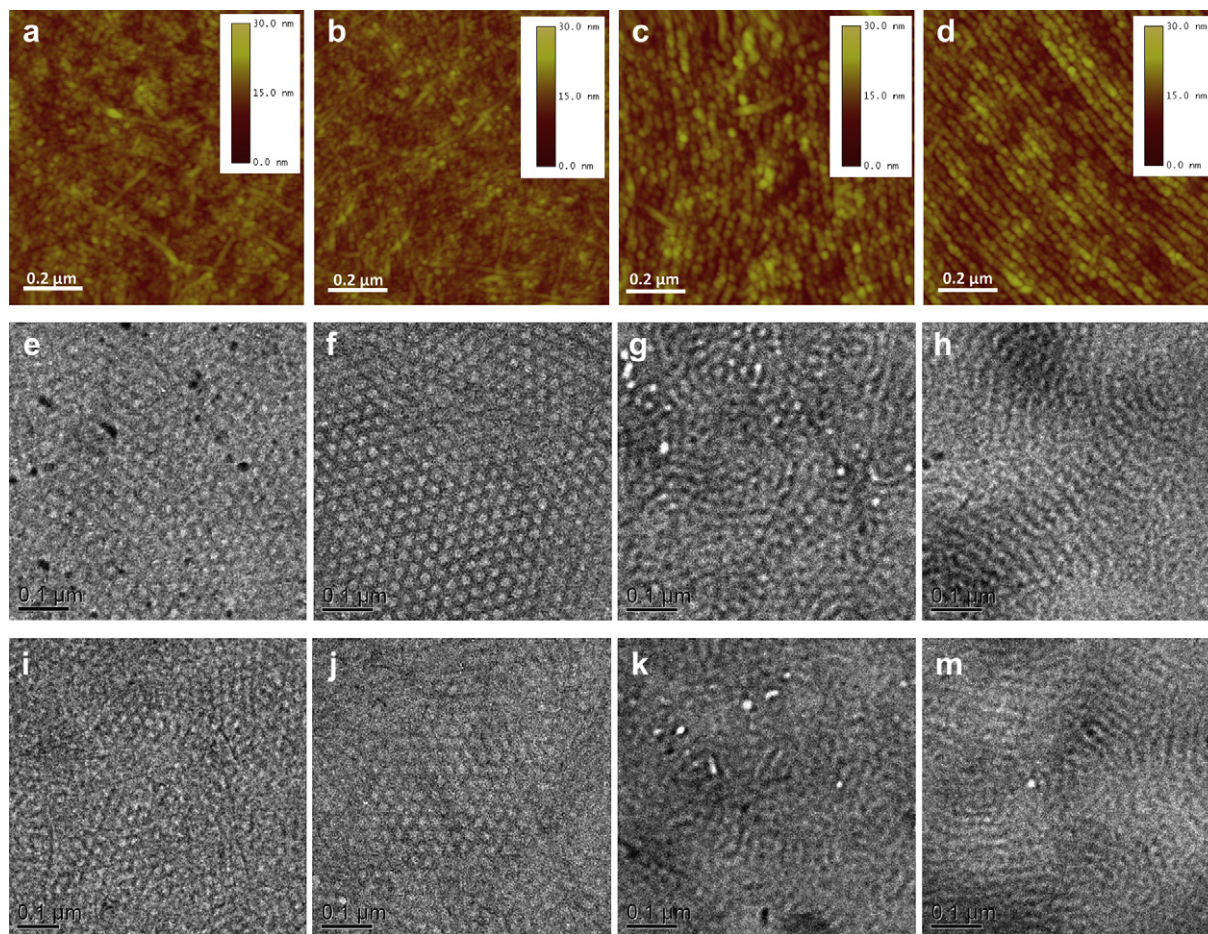


Fig. 4. AFM and TEM images of PS-b-P4VP/POAA thin film blends after solvent annealing in benzene/NMP vapor mixture with different volume ratios: (a, e) 0.95/0.05, (b, f) 0.97/0.03, (c, g) 0.98/0.02, (d, h) 0.99/0.01. (i), (j), (k), and (m) are TEM images of sample (e), (f), (g), and (h) tilted by 25°, respectively.

common body-centered cubic (BCC) lattice, then the image in Fig. 4f would correspond to the projections of the lattice in (111) directions. When tilting the specimen 25°, the lattice in (111) directions will slope and no projections of ordered lattice can be seen, so the TEM image become characterless as shown in Fig. 4j. It should be noted although large area of ordered arrays disappear in Fig. 4j, there are still ordered structures that can be seen, implying the defects exist in the interior ordered structure of the thin film. Fig. 4g shows the TEM micrograph of the thin film annealed in benzene/NMP (0.98/0.02, in volume) mixture vapor and Fig. 4k displays the image obtained by tilting the specimen by 25°. Similar to AFM result, a mixture of spherical and “pearl necklace” structure are observed in the TEM. Bright dots with a high contrast in the image imply the perpendicular “pearl necklaces” across the film thickness, indicating perpendicular and parallel pearl necklaces coexist in the thin film. From the image obtained by tilting the specimen 25°, no obvious difference from Fig. 4g is observed, demonstrating the phase structure consists in disordered mixed patterns of spherical and “pearl necklace” PS microdomains dispersed within P4VP/POAA matrix. For the thin film annealed in benzene/NMP (0.99/0.01, in volume) mixture, as shown in Fig. 4h, the TEM micrograph exhibits similar parallel “pearl necklaces” to AFM image. The “pearl necklace” microdomains where the dark region corresponds to a mixed phase of P4VP and POAA and the bright region corresponds to PS phase are found to pack in an ordered array with a period of 26 nm. The image of Fig. 4m obtained by tilting the specimen by 25° displays the same result to

that shown in Fig. 4h, confirming the formation of ordered parallel “pearl necklaces” in the interior structure of the thin film. It should be noted that although a very small quality of NMP in mixed benzene/NMP (0.99/0.01, in volume) could induce the formation of parallel “pearl necklace” structure in PS-b-P4VP/POAA film, pure benzene vapor annealing cannot work like that. Actually, solvent annealing in pure benzene vapor could not change the phase structure of PS-b-P4VP/POAA film due to weak mobility of PS-b-P4VP/POAA complex under pure benzene vapor.

Table 2 summarizes the size of microphase-separated structures of the blends thin film under different annealing condition. It can be seen that the spherical microphase-separated structures and PS microdomains of the blends thin film under different annealing condition nearly have the same diameter of ~19 nm, indicating the

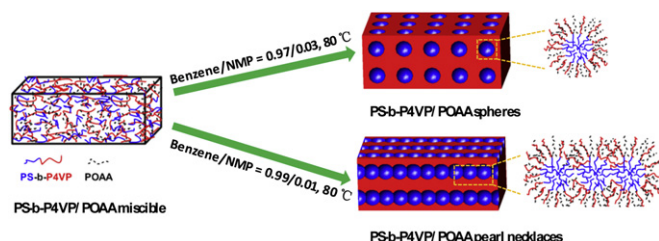
Table 2

Size of microphase-separated structures of PS-b-P4VP/POAA blends thin films after solvent annealing in NMP/benzene vapor mixture with different volume ratios of benzene to NMP.

Benzene/NMP ratios	diameter of spheres ^a (nm)	diameter of PS microdomains ^b (nm)
0.95: 0.05	19	19
0.97: 0.03	19	19
0.98: 0.02	18	15
0.99: 0.01	17	14

^a Determined by AFM images.

^b Determined by TEM images.



Scheme 1. Formation of ordered microphase-separated nanostructures in PS-b-P4VP/POAA thin film blends after solvent annealing in benzene/NMP vapor mixture with different volume ratios.

change of the annealing vapor composition has a little influence on the formation of microphase-separated nanostructure with PS microdomains dispersed in P4VP/POAA matrix and which is a thermodynamics-controlled process. It should be noted that the diameter of PS microdomains for the blends thin films annealed in benzene/NMP vapor with volume ratio of 0.98/0.02 and 0.99/0.01 is obvious smaller than that of the blends thin films annealed in benzene/NMP vapor with lower benzene content. It could be attributed to the fusion of PS microdomains during solvent annealing which leads to a distortion of PS microdomain in shape.

On the basis of the results above, by exposing the as-spun PS-b-P4VP/POAA thin films to benzene/NMP mixture vapor with proper volume ratios, ordered microphase-separated structures are obtained. As shown in Scheme 1, for the directly spin-coated thin film of PS-b-P4VP/POAA, a homogenous phase formed where POAA chains selectively interacted with P4VP blocks by strong interpolymer hydrogen-bonding. When the thin film was annealed in benzene/NMP (0.97/0.03, in volume) mixture vapor at 80 °C, ordered microphase-separated structure with PS spherical microdomains distributed within P4VP/POAA complexes matrix was obtained. In a A-b-B/C type block copolymer/homopolymer mixture, it is well established that the selectively distribution of C within B domains could induce the self-assembly structure of the A-b-B, since the incorporation of C chains will change the volume fraction of B relative to that of A [13,14,24]. In the case of PS-b-P4VP/POAA, the strong interpolymer hydrogen-bonding association between P4VP blocks and POAA homopolymer enriches the POAA chains selectively in the P4VP domain, leading to a significant increase of the volume fraction of P4VP domain relative to that of PS domain. For the PS-b-P4VP/POAA thin film blends during annealing in benzene/NMP vapor mixture, it is easily to achieve microphase separation structure with PS microdomains surrounded by P4VP/POAA matrix due to the substantial mobility and increased repulsion of PS blocks and P4VP/POAA complexes.

When the thin film was annealed in benzene/NMP (0.99/0.01, in volume) mixed vapor, ordered “pearl necklace” microphase-separated nanostructures from coalescence of spheres were obtained. Compared with the benzene/NMP mixture vapor with volume ratio of 0.97/0.03, the increasing benzene content in mixture vapor of benzene/NMP (0.99/0.01, in volume) vapor raise the total interfacial area between P4VP/POAA complexes and benzene vapor, and inevitably increase the interfacial energy of the system since benzene is poor solvent for P4VP/POAA complexes. To reduce the total interfacial energy in response to the increasing interfacial area, there is an increase in the sphere diameter. However, according to previous theory, this is thermodynamically unfavorable for some of the components of the free energy, as both the core-chain stretching and corona-chain repulsion in the spherical structure increase [25]. At this point, to reduce the total free energy of the system, cylinder morphology resulted from fusion of spheres formed, where the low degree of core-chain

stretching and corona-chain repulsion allows more chains to be incorporated into aggregates than spherical structure [26]. In the PS-b-P4VP/POAA system, although cylindrical nanostructures were not obtained the formation of “pearl necklace” structures from coalescence of spheres could also reduce the total free energy in response to the increasing interfacial area. It should be noted that the increasing volume ratio of PS domains due to swelling of PS core-chains by benzene vapor also contributed to the formation of “pearl necklace” nanostructures. The resultant pearl necklaces were arranged in an ordered array oriented parallel to the substrate, which could be ascribed to the preferential interaction of P4VP/POAA phase with substrate,

4. Conclusion

Ordered self-assembly structures of PS-b-P4VP/POAA blends in thin film where POAA chains selectively interact with P4VP blocks by strong interpolymer hydrogen-bonding, were prepared assisted with solvent annealing. By exposing PS-b-P4VP/POAA thin film blends to benzene/NMP (0.97/0.03, in volume) vapor mixture at 80 °C, ordered microphase-separated structures with PS spherical microdomains distributed within P4VP/POAA complexes matrix were obtained. Furthermore, by changing volume ratio of benzene to NMP in the vapor mixture, different ordered self-assembly structures of the thin film could be achieved. When the thin film was annealed in benzene/NMP (0.99/0.01, in volume) vapor at 80 °C, “pearl necklace” PS microdomains resulted from coalescence of PS spheres due to increasing PS-selectivity of the mixture vapor, formed a packed array oriented parallel to the film surface. However, for the thin film annealed at 80 °C without solvent environment, no obvious microphase separation was observed.

Acknowledgements

The authors would like to acknowledge the financial support of the important direction project for the knowledge innovative engineering of Chinese Academy of Sciences (Grant No.KGCX3-SYW-205) and the financial support of the National 973 project of China (2007CB607601).

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