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PAPER

Microdomain control in block copolymer-based supramolecular thin films through varying the grafting density of additives†

Chih-Hung Lee and Shih-Huang Tung*

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It is well known that the supramolecular assembly of block copolymers with associated low-molecular-weight additives leads to rich phase behaviors in both bulk and thin films. In this study, we demonstrate that the supramolecular assembly is also an efficient approach to control the microdomain orientation in block copolymer thin films. We investigated the effect of the content of low-molecular-weight additives on the microdomain orientation in supramolecular thin films formed by poly(styrene)-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) with hydrogen-bonded 3-pentadecylphenol (PDP) and found that at low grafting density of PDP onto P4VP chains, the PS microdomains are parallel to the surface, while above a critical grafting density, the orientation is switched to be perpendicular. Such orientation transitions are observed for both cylindrical and lamellar structures, as confirmed by AFM, TEM and GISAXS. We propose that the microdomain orientation is governed by the combining effect of interfacial energy and the spatial distribution of additive molecules that varies with grafting density.

Introduction

Block copolymers composed of covalently end-linked homopolymers can phase-separate into microdomains that form a variety of regular nanostructures.¹ Particularly, block copolymer thin films have drawn much attention due to their adjustable microdomain orientation and possible highly ordered arrays of microdomains that render the films potential for applications ranging from nanostructured templates to biosensors and electronic devices.^{2–4} In thin films with nano-scale thicknesses, the block copolymer chains are confined in a nearly 2-dimensional space where the interactions at film–substrate and film–air interfaces are critical in determining the spatial arrangements of microdomains and in ultra-thin films, such interactions can even lead to different microphase separation behaviors from those in bulk.⁵ Thus, techniques based on surface modifications that either tune the interfacial energies or impart more confinements, such as chemical treatments^{6–11} or topographical patterning on substrates,^{12–15} have been frequently used to control the orientation and microdomain ordering. Other successful techniques include external mechanical or electrical forces,^{16,17} solvent annealing^{18–21} and temperature gradients.²²

The incorporation of liquid crystal components covalently grafted onto one block of the copolymer has also been shown as

a technique to manipulate the orientation of microdomains in thin films.^{23–25} The liquid crystal components form smectic layers and it is the orientation of the smectic layers that governs the orientation of block copolymer microdomains since the microdomains prefer to be orthogonal to the smectic layers. Verploegen *et al.* have shown that in thin films with cylindrical microdomains embedded in matrices comprised of the smectic layers, the cylindrical microdomains are parallel to the substrate at low grafting density of liquid crystal components and they are switched to be perpendicular as the grafting density increases.²⁵ This method requires no surface modification to achieve orientation control and it allows for the introduction of functional elements grafted onto the systems. However, from the standpoint of orientation control, the synthesis of such block copolymers is relatively complicated and the adjustment of grafting density is not so flexible, making this method a challenge to conduct practically.

The synthetic challenges can be circumvented by adopting a supramolecular strategy: the synergistic assemblies of block copolymers and low-molecular-weight additives pioneered by Ikkala and ten Brinke where additives are associated with one block of the copolymers *via* secondary interactions, such as hydrogen bonding, electrostatic interactions or metal coordination.^{26–29} The versatile block copolymer-based supramolecular assemblies have led to a rich library of hierarchical structures. Since it does not require creating covalent bonds between copolymers and additives, the fabrication of these systems is simple, energy saving and various functional additives can be easily incorporated.^{30–32} Recently, in addition to bulk morphology, an increasing number of studies have focused on supramolecular thin films and the effects of the low-molecular-weight additives on the microdomain orientation have been discussed.^{33–41} However, due

Institute of Polymer Science and Engineering, National Taiwan University, Taipei, 10617, Taiwan. E-mail: shtung@ntu.edu.tw

† Electronic supplementary information (ESI) available: The *in situ* measurements of film thicknesses during solvent annealing, the TEM images of bulk PS(20000)-*b*-P4VP(17000)(DBSA)_{0.5} and PS(20000)-*b*-P4VP(17000)(DBSA)_{1.0}, and the AFM images of a PS(40000)-*b*-P4VP(5600)(PDP)_{2.5} thin film. See DOI: 10.1039/c1sm05334e

to different additives and experimental conditions used, the results were usually interpreted on a case-by-case basis.

The bulk morphology of supramolecules formed by poly(styrene)-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) with hydrogen-bonded 3-pentadecylphenol (PDP) onto P4VP block has been widely studied, as shown in Fig. 1.²⁹ The addition of PDP alters the relative volume fraction of each component, therefore causing a morphological transition depending on the amount of PDP added. Furthermore, the comb-like P4VP(PDP) complexes stack into lamellar structures other than block copolymer microdomains, which then gives rise to various hierarchical structures. Their thin film morphologies have also been investigated recently.^{37–39} In addition to the morphological transition found in the bulk sample, it has been shown that there is a strong correlation between the microdomain orientation in thin films and the fraction of P4VP(PDP).³⁹ At a low fraction of P4VP (PDP), the block copolymer lamellar microdomains are oriented parallel to the surface while above a critical fraction of P4VP (PDP), the PS cylinders or lamellae are oriented normal to the surface with P4VP(PDP) small lamellae oriented parallel to the surface. However, the mechanism of such an orientation switch is still not fully understood.

In this work, we investigate the effect of PDP, specifically the grafting density, on the microdomain orientation in PS-*b*-P4VP thin films and we focus on two supramolecules which form PS cylinders and lamellae, respectively. We found that the parallel orientation of cylindrical and lamellar microdomains at low grafting density of PDP can both be driven to be perpendicular as the grafting density increases and the critical density, *i.e.* the density where the switch of orientation occurs, is higher for lamellae. Similar phenomenon can also be found in supramolecules of PS-*b*-P4VP electrostatically bonded with dodecylbenzenesulfonic acid (DBSA) for cylindrical microdomains. Thus, this is a common effect for both block copolymer-based supramolecules and block copolymers with covalently-bonded side-chain liquid crystal components as described above. The incorporation of side chains either by primary or secondary bonds is an efficient way to control the microdomain orientation as well as to impart functionalities in block copolymer thin films. The advantage of supramolecular systems is that they can be fabricated simply by physical mixing and if the additives need to be removed, they can be easily washed away by proper solvents.

Experimental section

Materials

PS(40000)-*b*-P4VP(5600) (PDI = 1.09) and PS(20000)-*b*-P4VP (17000) (PDI = 1.08) were purchased from Polymer Source Inc.

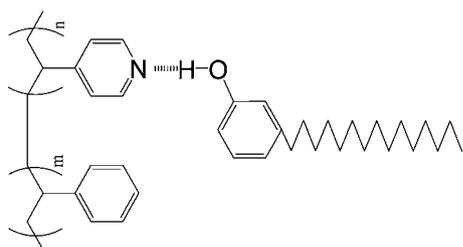


Fig. 1 Chemical structure of PS-*b*-P4VP(PDP) supramolecules.

3-*n*-Pentadecylphenol (PDP) (95%) and dodecylbenzenesulfonic acid (DBSA) (95%) were purchased from Sigma-Aldrich. Chloroform was purchased from Mallinckrodt Chemicals. All chemicals were used as received.

Sample preparation

The characteristics of all samples used in this paper are listed in Table 1. The block copolymer, PS-*b*-P4VP, was firstly dissolved in chloroform to form 1%–2% (wt/v) stock solutions. The desired amount of PDP or DBSA was also dissolved in chloroform. The PS-*b*-P4VP solution was then added drop-wise to the PDP or DBSA solution, followed by stirring for at least 2 days. Bulk samples were prepared by placing the solutions in Teflon beakers covered by an inverted dish and chloroform was evaporated slowly at room temperature for several days. Samples were further dried and annealed for 2 days in a vacuum oven at 100 °C for PDP-based samples or 150 °C for DBSA-based samples and pure block copolymers. Thin films were prepared by spin-coating the mixed solutions onto silicon wafers at spinning speeds between 1000 and 3000 rpm. Sample thicknesses were measured using a Filmetrics™ F20 interferometer. For solvent annealing, PDP-based thin films were placed together with a beaker of 40 ml chloroform at 22 °C for 48 h inside an inverted dish (170 Dia. × 90 H mm) on which a weight ~2 kilograms was loaded. DBSA-based thin films were annealed under a higher vapor pressure: films were inversely stuck on the cap of a sealed jar (250 ml) with the presence of liquid chloroform in the jar for 4 h. The swelling ratios, *i.e.* the thickness ratio of swollen films to original films, are about 1.5 for PDP-based thin films and 2.4 for DBSA-based thin films, which were determined from the *in situ* measurements of film thicknesses during annealing, as shown in Fig. S1 (ESI†).

Scattering

Small-angle X-ray scattering (SAXS) was conducted on beamline BL23A1 in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. A monochromatic beam of $\lambda = 1.240 \text{ \AA}$ was used. The scattering intensity profiles were reported as the plots of the scattering intensity I vs. the scattering vector q , where $q = (4\pi/\lambda) \sin(\theta/2)$, θ is the scattering angle. Grazing incidence small-angle X-ray scattering (GISAXS) was also conducted on beamline BL23A1 in NSRRC, with a wavelength of 1.240 Å. The scattering patterns were collected on a Mar-CCD with a diameter of 165 mm.⁴²

AFM and TEM imaging

Atomic force microscopy (AFM) was performed on a Multi-Mode AFM system with a Nanoscope 3D controller (Digital Instruments) in tapping mode. The spring constant of the cantilever (Nanosensor PPP-NCHR) was $\sim 42 \text{ N m}^{-1}$ with a resonant frequency $\sim 330 \text{ kHz}$. Bulk samples prepared for transmission electron microscopy (TEM) were embedded in resin and cured at 60 °C overnight and then were sectioned to a thickness $\sim 80 \text{ nm}$ using a diamond knife and transferred to copper grids. To prepare thin film samples for cross-sectional TEM imaging, a thin layer of platinum was sputtered onto the surfaces of thin films and then the films were attached to epoxy resin and cured at room temperature for 2 weeks. The substrate

Table 1 Characteristics of samples^a

Sample	x	f_{comb} (wt%)	Morphology (room temp.)	
			Bulk	Thin film
PS(20000)- <i>b</i> -P4VP(17000)(PDP) _{x}	0	45.9	lamella	lamella
	0.5	67.5	cylinder	cylinder
	0.8	73.8	cylinder	cylinder + \perp
	1.0	76.8	cylinder	cylinder \perp
PS(40000)- <i>b</i> -P4VP(5600)(PDP) _{x}	0	12.2	sphere	sphere
	1.0	35.3	lamella	lamella
	1.8	46.5	lamella	lamella + \perp
	2.5	53.6	lamella	lamella \perp
	3.0	57.6	lamella	lamella \perp

^a x : molar ratio of PDP to 4VP, f_{comb} : weight fraction of P4VP(PDP), ||: parallel to the surface, \perp : perpendicular to the surface.

was peeled off from the embedded films after the cured epoxy cubes were dipped into liquid nitrogen. The embedded films were then microtomed at room temperature. The thin sections were exposed to iodine vapor for 2 h that selectively stains the P4VP block to enhance the contrast. TEM images were collected on a Joel JEM-1230 transmission electron microscope at an accelerating voltage of 100 kV.

Results and discussion

PS(20000)-*b*-P4VP(17000)(PDP) _{x} systems

Here x denotes the molar ratio of PDP to 4VP units. The TEM images and SAXS data of bulk samples with $x = 0, 0.5$ and 1.0 are shown in Fig. 2. For the sample without PDP ($x = 0$), PS and P4VP blocks phase-separate into lamellar microdomains due to an approximately symmetric chain architecture, shown in Fig. 2a. After PDP is added and associated with P4VP chains, the weight fractions of P4VP(PDP) _{x} (f_{comb}) are increased and the morphologies are simultaneously changed. The f_{comb} for $x = 0.5$ and 1.0 are 67.5% and 76.8%, respectively, and both supramolecules form PS cylinders embedded in P4VP(PDP) matrices, shown in Fig. 2b and 2c. The relative positions of diffraction peaks of SAXS profiles shown in Fig. 2d are in order of 1 : 2 : 3 : 4 for $x = 0$ and 1 : $\sqrt{3}$: 2 : $\sqrt{7}$ for $x = 0.5$ and 1.0 , conforming the morphological transition from lamella to cylinder. The lamellar period for $x = 0$ are 37.8 nm and the periods of hexagonally-packed cylinders are 32.4 nm and 34.0 nm for $x = 0.5$ and 1.0 , respectively. The distinct diffraction peaks at $q = 0.16$ that result from the lamellar stacking of P4VP(PDP) comb-like chains correspond to a spacing of 3.9 nm. Note that this diffraction peak splits for $x = 1.0$, which is attributed to the crystallization of part PDP molecules.⁴³ In such supramolecules, the large-scaled PS cylinders are embedded in matrices with small-scaled P4VP(PDP) lamellae, *i.e.* a hierarchical cylinder-within-lamella structure.

We then discuss the morphologies of supramolecular assembly in thin films. Although both the supramolecules with $x = 0.5$ and 1.0 self-assemble into PS cylinders in P4VP(PDP) matrices, their thin film morphologies from AFM are very different. In Fig. 3a, a PS(20000)-*b*-P4VP(17000)(PDP)_{0.5} thin film ~ 75 nm in thickness shows a finger-like pattern on the surface, which could be either PS cylinders parallel to the surface or lamellae perpendicular to the surface. To clarify the structure throughout the

film, a cross-sectional TEM image was taken, shown in Fig. 3b. The deep dark layer in the image is the sputtered platinum and the film-platinum interface is originally the film-air interface. The sample was stained with iodine so that the brighter spots are the cross-sections of PS cylinders while the darker matrix is made up of P4VP(PDP). It clearly shows that PS(20000)-*b*-P4VP(17000)(PDP)_{0.5} phase-separates into PS cylinders and the cylinders are parallel to the surface in thin films. The morphology of the thin film was also probed by GISAXS. Fig. 3c shows the 2D GISAXS pattern at an incident angle of 0.27° , where diffraction rods are observed along both q_z and q_y axes. Such a spot-like pattern instead of diffraction rings demonstrates that the microdomains in the thin film are oriented. The q_y scan at $q_z = 0.156 \text{ \AA}^{-1}$ are plotted in Fig. 3d. The first-order peak at $q_y = 0.0170 \text{ \AA}^{-1}$ corresponds to a spacing of 36.9 nm, which is the period of parallel cylinders. The q_z scan at $q_y = 0.018 \text{ \AA}^{-1}$, also

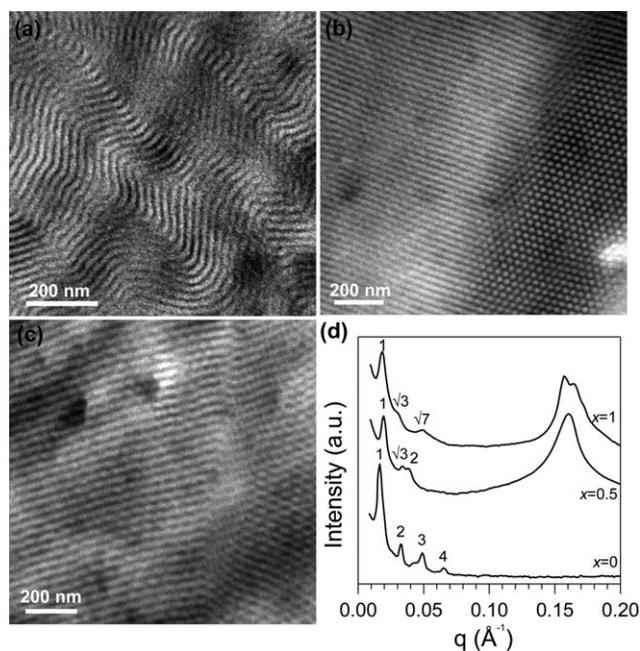


Fig. 2 TEM images of PS(20000)-*b*-P4VP(17000)(PDP) _{x} bulk samples: (a) $x = 0$, lamellar structure, (b) $x = 0.5$, PS cylinders, and (c) $x = 1.0$, PS cylinders. (d) SAXS profiles of PS(20000)-*b*-P4VP(17000)(PDP) _{x} bulk samples.

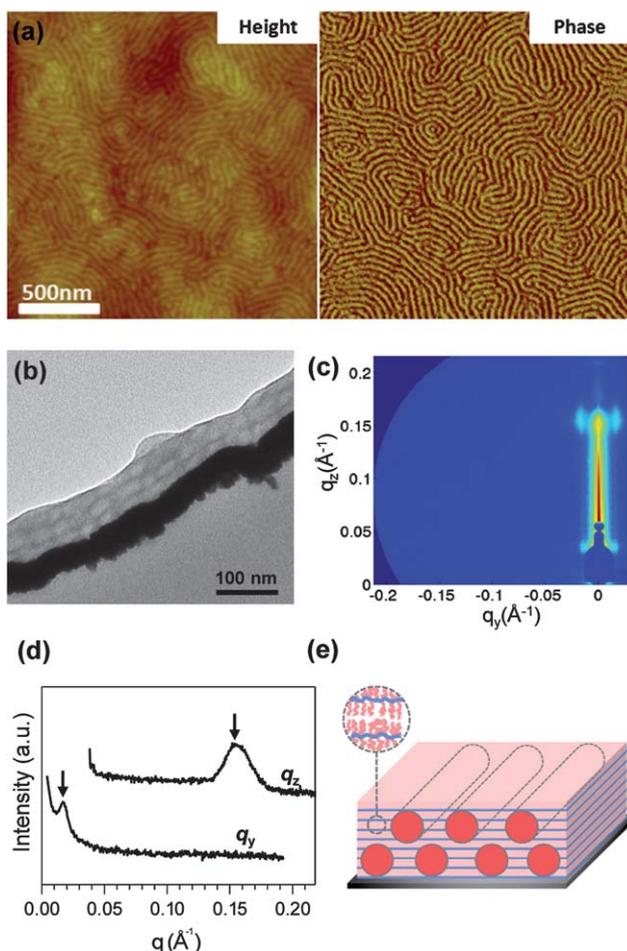


Fig. 3 Structure characterization of PS(20000)-*b*-P4VP(17000)(PDP)_{0.5} thin film, ~75 nm in thickness: (a) AFM images with z scale 20 nm for height and 20° for phase, (b) cross-sectional TEM image, (c) GISAXS pattern, (d) q_y scan at $q_z = 0.156 \text{ \AA}^{-1}$ and q_z scan at $q_y = 0.018 \text{ \AA}^{-1}$ extracted from (c), and (e) schematic illustration of proposed structure. Both the PS cylinders and P4VP(PDP) lamellae are parallel to the surface.

plotted in Fig. 3d, shows a peak at $q_z = 0.155 \text{ \AA}^{-1}$, corresponding to a period of ~4.1 nm. This peak is given by the P4VP(PDP) lamellae and more importantly, the appearance of the diffraction rod along q_z indicates that the P4VP(PDP) lamellae are parallel to the surface. In summary, by combining AFM, TEM and GISAXS results, the large- and small-scaled microdomains in PS (20000)-*b*-P4VP(17000)(PDP)_{0.5} thin films are both parallel to the surface, as shown in Fig. 3e.

The AFM images of a PS(20000)-*b*-P4VP(17000)(PDP)_{1.0} thin film ~66 nm in thickness are shown in Fig. 4a. The surface is featured with hexagonally-packed round domains, which could be either PS spheres or PS cylinders standing on the substrate. Further investigation by cross-sectional TEM, shown in Fig. 4b, reveals alternating bright and dark strips representing PS cylinders and P4VP(PDP) matrix, respectively, confirming that PS blocks form cylindrical domains perpendicular to the surface. Fig. 4c shows the GISAXS pattern at an incident angle of 0.27°. Although the orientation of PS cylinders is different from that in PS(20000)-*b*-P4VP(17000)(PDP)_{0.5} films, the GISAXS pattern looks similar, *i.e.* diffraction rods are observed along both q_y and

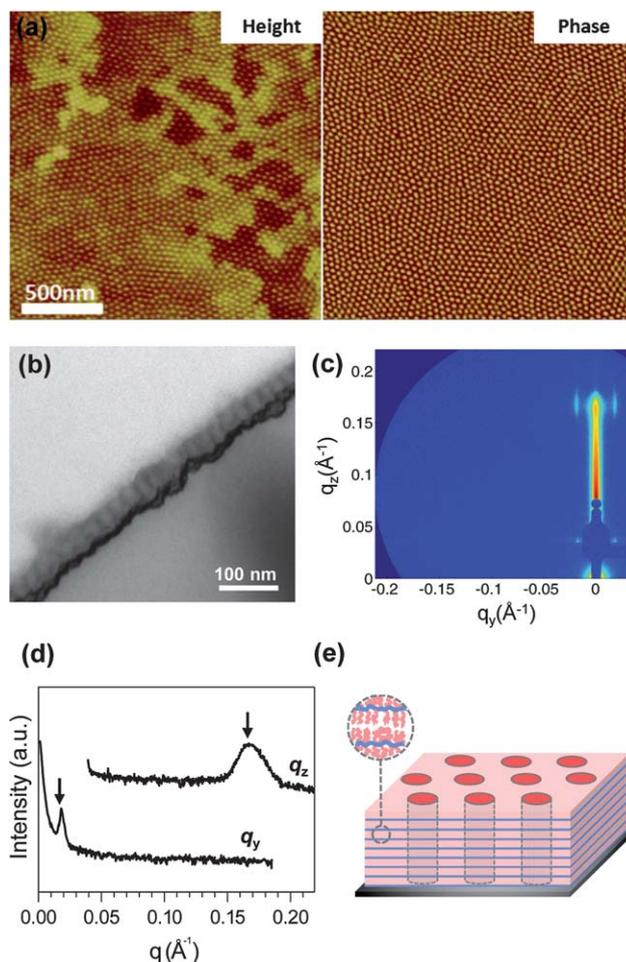


Fig. 4 Structure characterization of PS(20000)-*b*-P4VP(17000)(PDP)_{1.0} thin film, ~66 nm in thickness: (a) AFM images with z scale 10 nm for height and 15° for phase, (b) cross-sectional TEM image, (c) GISAXS pattern, (d) q_y scan at $q_z = 0.167 \text{ \AA}^{-1}$ and q_z scan at $q_y = 0.018 \text{ \AA}^{-1}$ extracted from (c), and (e) schematic illustration of proposed structure. The P4VP(PDP) lamellae are parallel to the surface while the PS cylinders are perpendicular to the surface.

q_z axes. The q_y scan at $q_z = 0.167 \text{ \AA}^{-1}$, plotted in Fig. 4d, shows a first-order peak at $q = 0.0182 \text{ \AA}^{-1}$, corresponding to a spacing of 34.5 nm, which is the period of perpendicular PS cylindrical microdomains. The q_z scan at $q_y = 0.018 \text{ \AA}^{-1}$, also plotted in Fig. 4d, shows a diffraction peak at $q_z = 0.167$, corresponding to a period of ~3.8 nm, originated from the P4VP(PDP) lamellae oriented parallel to the surface. Thus, in PS(20000)-*b*-P4VP(17000)(PDP)_{1.0} thin films, the large-scale PS cylindrical microdomains and the small-scale P4VP(PDP) lamellae are orthogonal, as shown in Fig. 4e. It has been known that the orientation of microdomains in block copolymer thin films is dependent on film thickness. In most cases, there is a preferential interaction between one of the blocks and substrate, which generally leads to a parallel arrangement of microdomains. However, if the thickness and the nature period of microdomains are incommensurate, a perpendicular arrangement may occur.⁴⁴ In the present case, we have examined a series of thicknesses under 150 nm and the perpendicular microdomains were consistently observed, indicating that the orientation is thickness-independent.

The above results reveal an interesting orientation transition of cylindrical microdomains: with lower grafting density of PDP, *i.e.* $x = 0.5$, the PS cylinders are parallel to the surface, while with more PDP, *i.e.* $x = 1.0$, the PS cylinders are forced to stand on the surface, though in both cases the P4VP(PDP) lamellae are parallel to the surface. As the content of PDPs is in the middle, a mixture of parallel and perpendicular cylinders is observed, which is demonstrated in a PS(20000)-*b*-P4VP(17000)(PDP)_{0.8} thin film shown in Fig. S2 (ESI†). The question now is why the grafting density of PDP can change the orientation of microdomains. To explain that, we firstly discuss why the comb-like P4VP(PDP) lamellae tend to be parallel to the surface. Due to the hydrophilic nature of the silicon substrate, the relatively hydrophilic P4VP blocks has preferential interactions with the substrate, while the hydrophobic alkyl tails of PDP incline to expose to air. The former force attracts the P4VP chains to lie on the substrate and the later force results in a PDP layer at the film–air interface that prevents P4VP from contacting air. These two forces, from the bottom and the top of thin films respectively, compel the P4VP(PDP) layers to be parallel to the interfaces and then the stacking is progressively extended into thin films.³⁶ Note that PDP chains are oriented either up or down in the lamellae, as shown in Fig. 3e and 4e, which is an important factor that controls the orientation of PS cylinders, as described below.

It has been shown that in side-chain liquid crystal block copolymer systems where cylindrical microdomains are formed, the side chain molecules prefer to orient parallel to the long axis of the cylinders to prevent a crowding of side chains near the cylinder interfaces due to the non-planar interfaces of cylinders and thus achieve interface stabilization.^{45,46} Similar arrangements have also been found in the self-assembly of coil–comb block copolymer supramolecules in bulk.^{47,48} A crowding situation that occurs when side chains are oriented perpendicular to the long axis of cylinders is illustrated in Fig. 5. As a result, the orientations of the large-scale cylinders and the small-scale lamellae prefer to be orthogonal. In thin films, we have seen that the P4VP (PDP) lamellae tend to be parallel to the surface. The PS cylinders should then be forced to be perpendicular to the surface if the effect described above can overtake the preferential P4VP–substrate interactions that prevent PS from contacting the substrate. This successfully explains the morphology in PS (20000)-*b*-P4VP(17000)(PDP)_{1.0} thin films where the high binding ratio of 4VP with PDP provides sufficient driving forces to direct the orientation of PS cylinders, shown in Fig. 4e. In the case of PS(20000)-*b*-P4VP(17000)(PDP)_{0.5}, however, since the

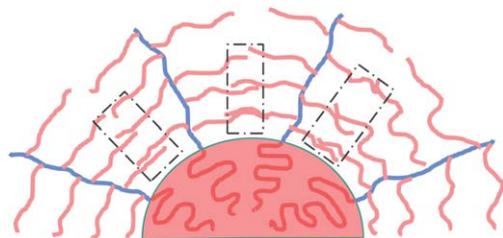


Fig. 5 In the case that side chains are oriented perpendicular to the long axis of cylinders, the side chain molecules will be crowded near the interfaces of cylinders. Thus, it will be more stable if the cylinders and the lamellae of comb-like blocks are orthogonal, as shown in Fig. 4e.

grafting density of PDP is low, there is more room to accommodate each PDP molecule and the crowding effect near the cylinder interfaces could be greatly alleviated. Also, due to a significant fraction of 4VP units unbound with PDP, there should be more 4VP units that can stick on the substrate. In other words, although the P4VP(PDP) lamellae are parallel, the preferential P4VP–substrate interactions dominate over the interface stabilization effects and thus cause a parallel orientation of PS cylinders. Similar results have been reported for side-chain liquid crystal block copolymers in thin films, where the content of side-chain mesogens governs the microdomain orientation.²⁵ We demonstrate here that it can be accomplished simply by a supramolecular strategy using common small molecules.

In addition to PDP, dodecylbenzenesulfonic acid (DBSA) is commonly used to form comb-like supramolecules *via* stronger electrostatic interactions with P4VP chains, instead of weak hydrogen bonding between PDP and P4VP, shown in Fig. 6a.⁴⁷ The capability of DBSA to alter the morphology of block copolymers is analogous to that of PDP. We thus characterized PS(20000)-*b*-P4VP(17000)(DBSA)_{*x*} thin films to see if the results described above can be consistently observed. In both bulk

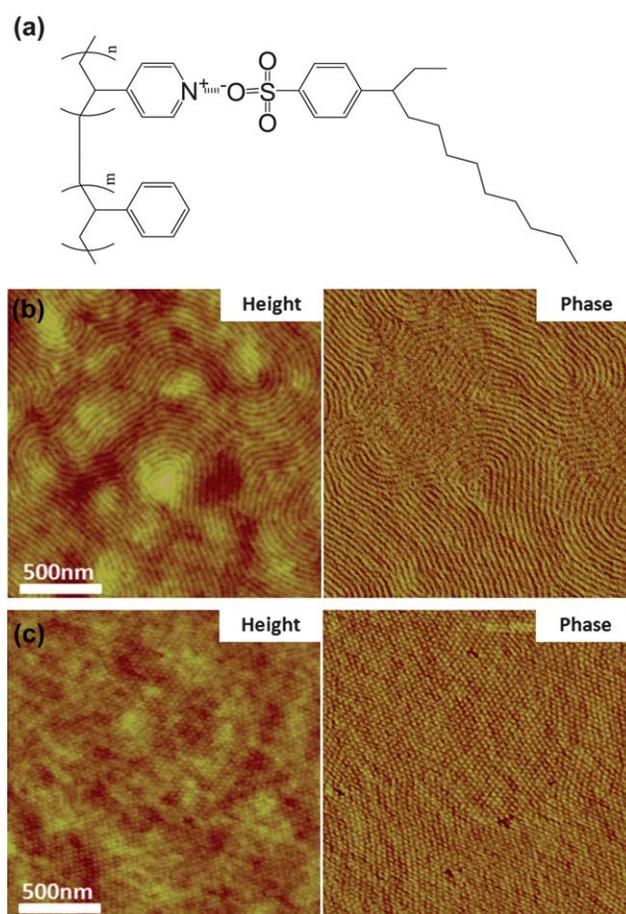


Fig. 6 (a) Chemical structure of PS-*b*-P4VP(DBSA) supramolecules. AFM images of PS(20000)-*b*-P4VP(17000)(DBSA)_{*x*} thin films: (b) $x = 0.5$, ~ 97 nm in thickness, showing parallel PS cylinders. The z scale is 10 nm for height and 20° for phase. (c) $x = 1.0$, ~ 103 nm in thickness, showing perpendicular PS cylinders. The z scale is 20 nm for height and 30° for phase.

samples with $x = 0.5$ and 1.0 , PS blocks form cylindrical microdomains in P4VP(DBSA) matrices, shown in Fig. S3a and S3b (ESI†). As spun-cast into thin films, resembling the PS-*b*-P4VP(PDP) systems, the PS cylinders are parallel to the surface for $x = 0.5$ while perpendicular to the surface for $x = 1.0$, shown in Fig. 6b and 6c. Note that a higher vapor pressure of annealing solvents is required to achieve ordered structures in PS-*b*-P4VP (DBSA) thin films possibly due to the lower mobility of P4VP (DBSA) blocks. The effect of grafting density on the orientation of cylindrical microdomains in thin films is similar for grafted additives with hydrophobic tails.

PS(40000)-*b*-P4VP(5600)(PDP)_{*x*} systems

We now turn our focus on PS(40000)-*b*-P4VP(5600)(PDP)_{*x*} systems, for which we intend to tailor the orientation of lamellar microdomains in thin films. The bulk morphologies characterized by TEM and SAXS are shown in Fig. 7. For pure PS(40000)-*b*-P4VP(5600), *i.e.* $x = 0$, P4VP is minor phase and forms spherical microdomains in PS matrices (Fig. 7a). As x increases to 1.0 , $f_{\text{comb}} = 35.3\%$, the PS and P4VP(PDP) blocks turn to be lamellae (Fig. 7b). The lamellar structure remains upon further increasing x to 3.0 ($f_{\text{comb}} = 57.6\%$). The morphology of a representative sample with $x = 2.5$ is shown in Fig. 7c, where we can see ordered lamellae with twin boundaries, which is an interfacial defect. The SAXS profiles of PS(40000)-*b*-P4VP(5600)(PDP)_{*x*} bulk samples are shown in Fig. 7d, where the relative positions of diffraction peaks are $1:\sqrt{2}:\sqrt{3}:2$ for $x = 0$ and $1:2:3:4$ for $x = 1.0, 2.0$ and 3.0 , confirming the spherical and lamellar microdomains, respectively. The obscure diffraction peaks for $x = 3$ reflect a less ordered lamellar structure possibly due to the large amount of excess PDP. Note that all the first-order peaks for $x \geq$

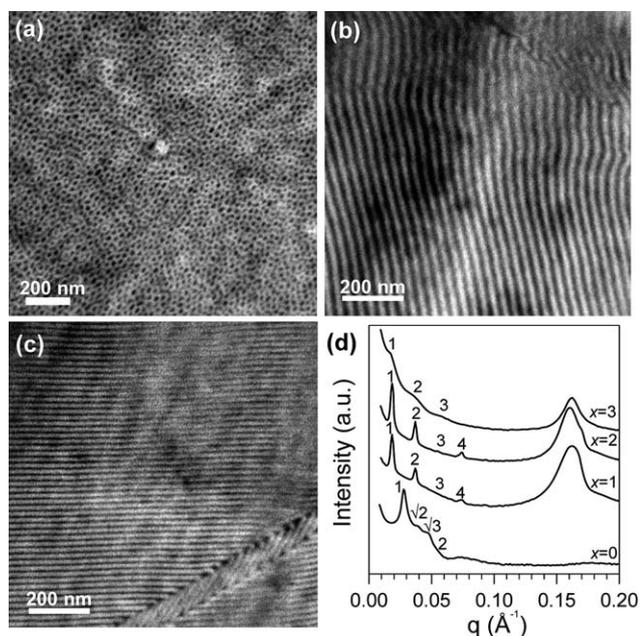


Fig. 7 TEM images of PS(40000)-*b*-P4VP(5600)(PDP)_{*x*} bulk samples: (a) $x = 0$, P4VP spheres, (b) $x = 1.0$, lamellar structure, and (c) $x = 2.5$, lamellar structure. (d) SAXS profiles of PS(40000)-*b*-P4VP(5600)(PDP)_{*x*} bulk samples.

1.0 are fixed at $q = 0.0185 \text{ \AA}^{-1}$, implying the periods of the lamellae remain 40.0 nm even though the content of PDP is increased by three times.

Fig. 8a shows the AFM images of a PS(40000)-*b*-P4VP(5600)(PDP)_{*x*} thin film $\sim 54 \text{ nm}$ in thickness. The surface of the film is basically featureless, with only a few small holes spreading on it. The smooth surface is characteristic of block copolymer thin films with lamellar microdomains oriented parallel to the surface. A P4VP(PDP) layer should be formed at the bottom of the film where the P4VP chains are in touch with silicon substrate. On the top of the film, the holes give a clue to determine what components on the surface. Carefully examining the topography profile (Fig. 8b) along the line shown in the height image of Fig. 8a, the depths of the holes are about $3\text{--}5 \text{ nm}$, which is approximately the period of P4VP(PDP) lamellae, $\sim 4 \text{ nm}$. It is well known that in block copolymer thin films with parallel lamellae, when film thicknesses and the natural period of lamellae are incommensurate, holes or islands may be formed on the surface and the height

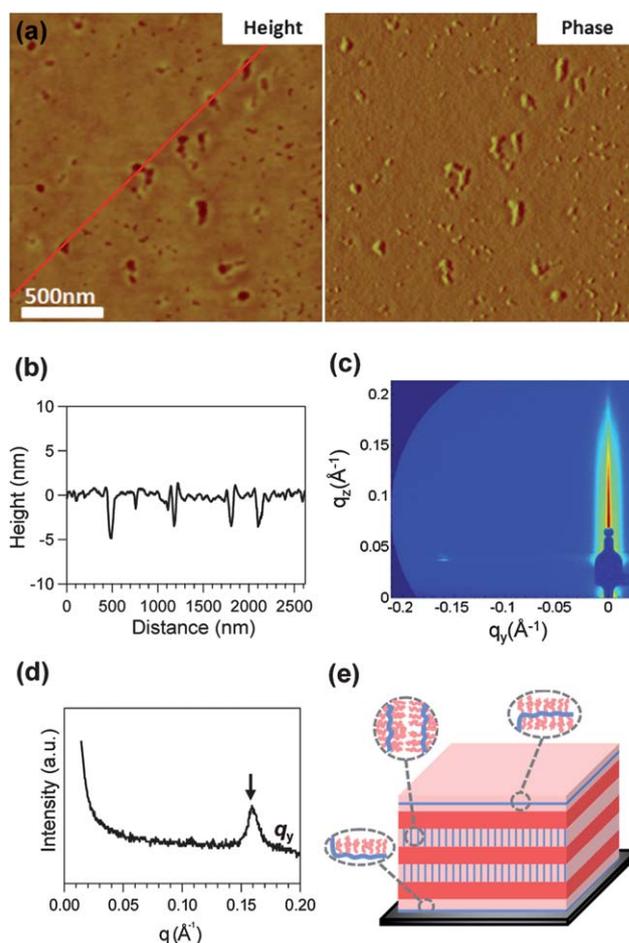


Fig. 8 Structure characterization of PS(40000)-*b*-P4VP(5600)(PDP)_{*x*} thin film, $\sim 54 \text{ nm}$ in thickness: (a) AFM images with z scale 20 nm for height and 50° for phase, (b) topography profile along the line in the height image of (a), (c) GISAXS pattern, (d) q_y scan at $q_z = 0.037 \text{ \AA}^{-1}$ extracted from (c), and (e) schematic illustration of proposed structure. The block copolymer lamellae are parallel to the surface while the P4VP (PDP) lamellae are oriented differently at the interfaces and inside the film.

of the holes or islands will be close to the natural period.^{5,49} Much similar to block copolymer microdomains, the incommensurability between the thicknesses of layers and the period of P4VP (PDP) lamellae may cause the formation of holes. Therefore, the layer on the top of the film should be formed by P4VP(PDP) lamellae and the lamellae are parallel to the surface, with alkyl tails of PDP exposed to air.²⁴ GISAXS was used to elucidate the internal structures of films, as shown in Fig. 8c and 8d. Diffraction rods, corresponding to a spacing of 3.9 nm, only appear along the q_y axis, which means that the majority of P4VP (PDP) lamellae in thin films are orientated perpendicular to the surface. In other words, the P4VP(PDP) lamellae inside the film that contact neither substrate nor air are orthogonal to PS layers. From the thermodynamics standpoint, such orthogonal arrangement is more stable since PDP can distribute evenly along the stretched P4VP chains. On the film–substrate and film–air interfaces, the parallel orientation requires P4VP chains to change direction, which may cause PDP to be too crowded around the turn points. Such an unfavorable crowding effect, however, can be overcome by the favorable P4VP–substrate and PDP tails–air interactions at $x = 1.0$. The structure of PS(40000)-*b*-P4VP(5600)(PDP)_{1,0} thin film is illustrated in Fig. 8e. Note that the diffraction rods of block copolymer-scale parallel lamellae are supposed to be observed along q_z axis. However, we are not able to see it. This is because the diffraction rod is out of the low- q limit in the q_z axis due to sample tilting when GISAXS experiments were conducted and also, there should be only a few parallel layers in such a thin film, which may not be sufficient to give sharp diffraction peaks.

As x increases above 2.5, the surface morphology is dramatically changed. In Fig. 9a, the AFM images of a PS(40000)-*b*-P4VP(5600)(PDP)_{3,0} thin film ~ 66 nm in thickness show finger-like patterns, where the curly stripes are the cross-sections of lamellae, *i.e.* the lamellae are perpendicular to the surface. The 2D pattern of GISAXS shown in Fig. 9b reveals diffraction rods at small q along q_y axis, together with the 1 : 2 relation of the diffraction peaks in q_y scan (Fig. 9c), confirming the perpendicular lamellar structure. Similar to PS(20000)-*b*-P4VP(17000)(PDP) _{x} cylindrical systems, the content of PDP can alter the orientation of lamellae as well, but the transition occurs at a higher x value. Note that the period of lamellae calculated from the GISAXS data, ~ 47.5 nm, is larger than that in bulk, which may be due to the swelling of microdomains during solvent annealing. Furthermore, no diffraction peak from small-scaled P4VP(PDP) lamellae is observed for $x = 3.0$, implying that the large amount of excess PDP may impede the regular stacking of P4VP(PDP) comb-like chains.⁵⁰ The proposed structure is illustrated in Fig. 9d. Similar perpendicular lamellae are formed in thin films with $x = 2.5$, whose AFM images can be found in Fig. S4 (ESI†). At $x = 1.8$ where the orientation is in transition, both parallel and perpendicular lamellae are observed, shown in Fig. 10a. This mixed morphology is supported by the GISAXS data (Fig. 10b and 10c), where the diffraction rods of P4VP (PDP) lamellae appear along both q_y and q_z axes, indicating that the P4VP(PDP) lamellae are oriented both parallel and perpendicular to the surface.

We now put forward plausible explanations for the observed dependence of microdomain orientation on the PDP content in PS(40000)-*b*-P4VP(5600)(PDP) thin films. Since the interfaces

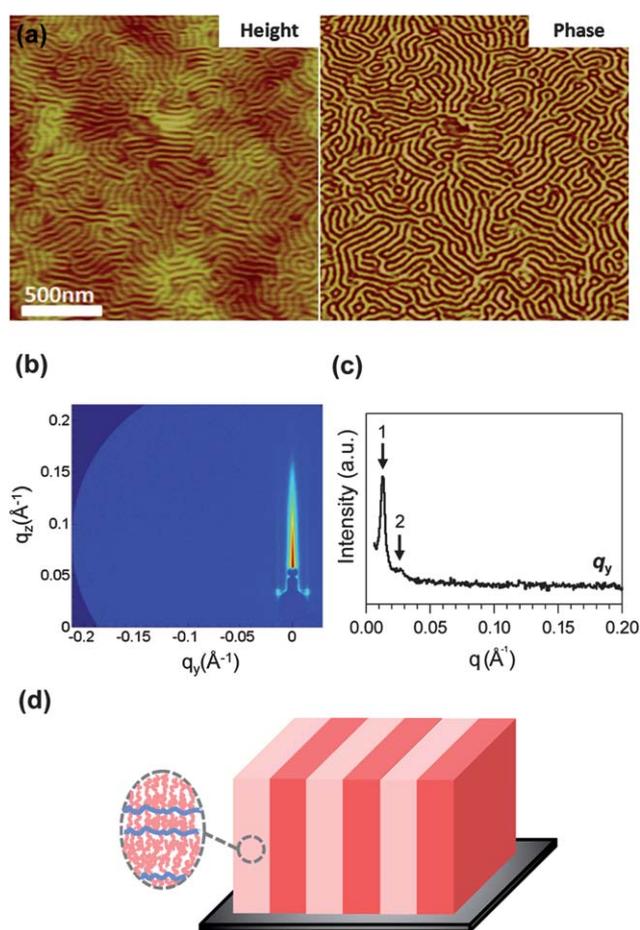


Fig. 9 Structure characterization of PS(40000)-*b*-P4VP(5600)(PDP)_{3,0} thin film, ~ 66 nm in thickness: (a) AFM images with z scale 10 nm for height and 20° for phase, (b) GISAXS pattern, (c) q_y scan at $q_z = 0.032 \text{ \AA}^{-1}$ extracted from (b), and (d) schematic illustration of proposed structure. The block copolymer lamellae are perpendicular to the surface while the P4VP(PDP) comb-like blocks are disordered.

between lamellae are planar, different from the non-planar interfaces between cylinders and matrices, and the P4VP(PDP) lamellae are not always parallel to the surface, the mechanism that describes the orientation transition in PS(20000)-*b*-P4VP(17000)(PDP) thin films is unsuited for lamellar systems. We note that the critical x value for orientation transition is much higher (>2.5) for lamellar systems, which means that a great amount of excess PDP are required to trigger the transition. Firstly, the excess PDP that locate in P4VP blocks reduces the preferential P4VP–substrate interaction and at high x , more PDP may distribute in PS blocks, both of which neutralize the interactions between substrate and each block. The neutralization of interfacial energies has been shown to induce perpendicular microdomains in block copolymer thin films.^{6,7} Secondly, it has been found that the more PDP are added into P4VP, the more stretched the P4VP chains.^{36,51} In other words, at high x , the crowding effect of PDP will be more severe around the turn points shown in Fig. 8e that are required to maintain the parallel P4VP(PDP) lamellae at the film–air and film–substrate interfaces. The unfavorable crowding effect is now too large to be overcome by the already reduced preferential interactions and

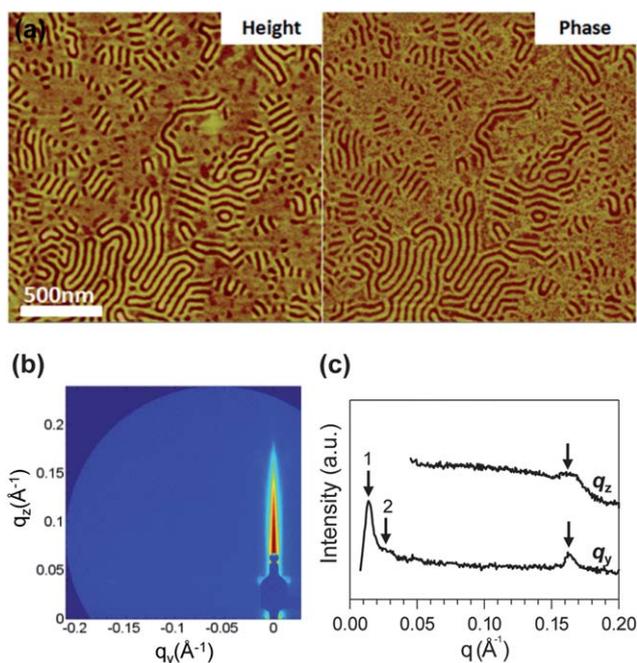


Fig. 10 Structure characterization of PS(40000)-*b*-P4VP(5600)(PDP)_{1.8} thin film, ~78 nm in thickness: (a) AFM images with z scale 10 nm for height and 60° for phase, (b) GISAXS pattern, and (c) q_y scan at $q_z = 0.038 \text{ \AA}^{-1}$ and q_z scan at $q_y = 0.014 \text{ \AA}^{-1}$ extracted from (b). The morphology is a mixture of perpendicular and parallel block copolymer lamellae.

the P4VP(PDP) comb-like chains tend to be stretched. To allow more PDP tail ends exposing to air and more P4VP chains contacting and stretching out along the hard substrate, *i.e.* nematic effect that may reduce entropic loss of stretched chains,^{52,53} the film adopts perpendicular rather than parallel lamellae at high x .

Conclusions

We have shown that the microdomain orientation in block copolymer thin films can be simply controlled by the incorporation of low-molecular-weight additives that bind one of the blocks. In both cylindrical and lamellar systems, as the content of low-molecular-weight additives is low, the orientation is parallel to the surface and it turns to be perpendicular as the content increases. A great amount of excess additives is required to achieve the orientation transition for lamellae. We propose that for the cylindrical systems, the perpendicular orientation is regulated by the tendency of the large-scaled cylinders to be orthogonal to the parallel small-scale lamellae formed by the comb-like chains at high grafting density, while for the lamellar systems, the perpendicular orientation is induced by the neutralization of interfacial energies as well as the stretching of polymer chains caused by the addition of a large amount of additives. This is a facial, highly efficient method to tailor the microdomain orientation in block copolymer thin films since the grafting density of such supramolecules can be simply adjusted by adding varying content of low-molecular-weight additives.

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