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# Highly ordered luminescent microporous films prepared from crystalline conjugated rod-coil diblock copolymers of PF-*b*-PSA and their superhydrophobic characteristics<sup>†</sup>

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We have successfully prepared three crystalline conjugated rod–coil diblock copolymers of poly[2,7-(9,9-dihexylfluorene)]-*block*-poly(stearyl acrylate) (PF-*b*-PSA), PF<sub>7</sub>-*b*-PSA<sub>64</sub>, PF<sub>7</sub>-*b*-PSA<sub>93</sub>, and PF<sub>7</sub>-*b*-PSA<sub>166</sub>, *via* the combination of a Suzuki coupling reaction and atom transfer radical polymerization. The crystalline comb-like PSA coil segment effectively formed the highly ordered microporous films through a "breath figure" (BF) process. On the other hand, the blue-emission band of the PF block was blue-shifting and became narrower as the PSA block was increased. The effects of block ratio, humidity, and solution concentrations on the porous structures were studied. The longer PSA block length, larger humidity, and higher copolymer concentration formed a more regular PF-*b*-PSA microporous film showed that all bubbles were independent and perfectly monodisperse with a pore diameter *ca*. 1.85 µm. Furthermore, a rod-*co*-valley-like structure exhibited superhydrophobicity (contact angle up to  $163 \pm 0.3^{\circ}$ ), which was obtained from the peeled skin layer of the ordered PF<sub>7</sub>-*b*-PSA<sub>166</sub> microporous surface. The experimental results revealed that multifunctional ordered microporous films could be successfully prepared from crystalline conjugated rod–coil block copolymers.

# 1. Introduction

Highly ordered microporous films have attracted extensive scientific interest because of the potential applications in patterned templates, photonic band gap, cell patterning, filtration membranes, and surface wettability.<sup>1–5</sup> "Breath Figures" (BF) process<sup>6,7</sup> represents a facile, simple, economic, and non-templated method for fabricating highly ordered microporous polymer films, including conjugated polymers,<sup>8–10</sup> rod–coil block copolymers,<sup>11–14</sup> star-branched polymers.<sup>15–18</sup> It uses a highly volatile solvent and an applied airflow under a humid environment, which leads to the water vapor condensing on the surface to form an ordered pore structure. The porous structure was controlled by the polymer architecture, molecular weight, and the casting condition. Several conjugated polymers were reported

to form a highly ordered hole array structure by the BF method,<sup>8-10</sup> including poly(*p*-phenyleneethynylene), poly(3-alkylthiophene), poly(9,9'-dialkylfluorene), and poly(*p*-phenylenevinylene). However, only limited linear conjugated rod–coil block copolymers were reported to form ordered microporous films, which used amorphous polystyrene coil.<sup>11–14</sup>

The formation of the ordered microporous films through the BF process is generally to prevent the coalescence of water droplets, which could be achieved by kinetic or thermodynamic control.<sup>19-21</sup> In the case of kinetic control, the higher segment density of star or comb-like polymers than the linear polymers facilitates the faster precipitation at the organic/water interface and thus the water droplets have no time to coalesce before the film solidification, such as star polystyrene or comb-like glycopolymer.<sup>15,16,18,20,21</sup> In addition, the ordered polymer structure could help the formation of the highly uniform porous structure. Thus, the proposed crystalline conjugated rod-coil block copolymers of poly[2,7-(9,9-dihexylfluorene)]-block-poly(stearyl acrylate) (PF-b-PSA) could represent ideal polymers for such application. Polyfluorenes have been widely studied due to their high luminescence yield and good charge-transporting characteristics, which may have potential applications for sensory or optoelectronic device applications. On the other hand, poly (stearyl acrylate) has comb-like, crystalline, physical cross-linking, and hydrophobic characteristics due to its long alkyl side

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<sup>†</sup> Electronic supplementary information (ESI) available: <sup>1</sup>H NMR spectra and GPC profiles of PF–Br, PF<sub>7</sub>-*b*-PSA<sub>64</sub>, PF<sub>7</sub>-*b*-PSA<sub>93</sub>, and PSA. TGA and DSC curves of studied copolymers at the heating rate of 20 °C min<sup>-1</sup> and under 10 °C min<sup>-1</sup> a nitrogen atmosphere. The top-view and cross-section SEM images of PF<sub>7</sub>-*b*-PSA<sub>166</sub> microporous film. WAXD intensity profiles of the microporous films, spin-coated films, and PSA powder. See DOI: 10.1039/c1sm05712j

chain group.<sup>22–24</sup> The structure of the comb-like PSA containing block copolymers would be similar to the star-shaped or hyperbranched coil polymers, which would benefit the formation of the ordered microporous films. Also, the crystalline PSA block could facilitate the stabilization of water droplets and result in a highly ordered microporous structure. Thus, it would be of interest to explore the synthesis and morphology of PF-*b*-PSA conjugated rod–coil block copolymers.

In this paper, we report the synthesis, morphology, and properties of three new crystalline conjugated rod-coil block copolymers of PF7-b-PSA64, PF7-b-PSA93, and PF7-b-PSA164, which were prepared by via the combination of a Suzuki coupling reaction and atom transfer radical polymerization (ATRP) (Scheme 1). The polymer structure, thermal properties, and photophysical properties of the block copolymers were studied. Next, the BF method was used to form highly ordered microporous structures. The effects of coil length, humidity, and concentration on the formation of the ordered porous film were studied. The surface morphology and interior structure of the ordered microporous film were characterized by field-emission scanning electron microscope (FE-SEM), two photon laser confocal microscope, and transmission-mode wide angle X-ray scattering (WAXS). Finally, a rod-co-valley-like structure was obtained from the peeled skin layer of the ordered microporous surface for exhibiting superhydrophobicity. The experimental results suggested the new crystalline PF-b-PSA could exhibit the multi-functionality of photoluminescence and a superhydrophobic surface.<sup>25-27</sup>

#### 2. Experimental section

#### Materials

Stearyl acrylate (SA, Polysciences, Inc.) was re-crystallized from an ethanol solution. 1,1,4,7,7-Pentamethyldiethylenetriamine, PMDETA (Acros, 99%), was used as received. CuBr (99%),

mers,  $PF_7$ -*b*-PSA<sub>n</sub> (n = 64, 93, 166).

2,7-dibromo-9,9-dihexylfluorene, 4-bromobenzyl alcohol, 2bromoisobutyryl bromide, tetrakis(triphenylphosphine)palladium(0), sodium carbonate methyl 2-bromopropionate (98%), chloroform, anisole, *N*,*N*-dimethylacetamide, and methanol were purchased from Aldrich Chemical Co. and used without further purification. Poly(2,7-(9,9-dihexylfluorene))-*block*-poly (methylmethacrylate) (PF<sub>7</sub>-*b*-PMMA<sub>810</sub>) was prepared according to our previous report.<sup>28</sup>

#### Synthesis of PF-b-PSA diblock copolymers

Synthesis of PF-b-PSA diblock copolymer is shown in Scheme 1. PF-Br macroinitiator with  $M_{\rm n}$  and PDI of 2610 and 1.61, respectively, was prepared via a Suzuki coupling reaction according to our previous report.<sup>29,30</sup> PF-b-PSA copolymers with different coil lengths were synthesized from PF-Br via ATRP. The preparation of PF7-b-PSA166 is exemplified below: a dry round-bottom flask with a magnetic stir bar was charged with the mixture of CuBr (14 mg, 0.1 mmol), PF-Br macroinitiator (258 mg, 0.1 mmol), SA (16.2 g, 50 mmol), PMDETA (21 µL, 0.1 mmol), and anisole (16 mL). The mixture was degassed by bubbling nitrogen to remove oxygen for 30 min, then immersed into an oil bath at 110 °C and stirred for 48 h. The polymerization was stopped by bubbling air into the crude solution. The mixture was passed through an Al<sub>2</sub>O<sub>3</sub> column to remove the copper catalyst. In the following, the reaction mixture was poured into methanol, precipitated, filtered and dried under vacuum at 40 °C to obtain PF7-b-PSA166 (2.82 g) as a light yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  (ppm): 0.86–0.90  $(3H, -CH_2CH_2(CH_2)_{15}CH_3), 1.21-1.34$   $(30H, -CH_2CH_2)$ 1.59-1.65 (2H, -CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>; (CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 2H, -CH<sub>2</sub>CH-), 1.89-1.96 (2H, -CH<sub>2</sub>CH-), 2.25-2.39 (1H, -CH<sub>2</sub>CH-), 3.99-4.13 (2H, -OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), and 7.25-7.84 (10H, fluorene aromatic protons and phenyl end group). The reaction conditions and molecular weight distributions of the three PF-b-PSA are listed in Table 1.

#### Synthesis of poly(stearyl acrylate) (PSA)

PSA were synthesized via ATRP and used methyl 2-bromopropionate as initiator. CuBr (14 mg, 0.1 mmol), methyl 2-bromopropionate (16.7 mg, 0.1 mmol), SA (4.86 g, 15 mmol), PMDETA (21  $\mu$ L, 0.1 mmol), and anisole (5 mL) were placed in a 25 mL dry round-bottom flask containing a magnetic stir bar. The mixture was degassed by bubbling nitrogen for 30 min, and placed in a 110 °C oil bath for 24 h. After removing metal catalyst by Al<sub>2</sub>O<sub>3</sub> column, the mixture was precipitated into methanol and dried under vacuum at 40 °C to obtain PSA as a white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  (ppm): 0.82– 0.90 (3H, -CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 1.17-1.36 (30H, -CH<sub>2</sub>CH<sub>2</sub> (CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 1.53–1.67 (2H, -CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>; 2H, -2.20-2.36 CH<sub>2</sub>CH-), 1.84-1.92 (2H,  $-CH_2CH_-$ ), (1H, -CH<sub>2</sub>C<u>H</u>-), and 3.92-4.10 (2H, -OC<u>H</u><sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>). Number-averaged molecular weight  $(M_p)$  and polydispersity index (PDI) estimated from GPC were 27000 and 1.38, respectively.



 Table 1
 Polymerization conditions, molecular weights, and thermal properties of PF7-b-PSA166 copolymers

Calculated composition	[M] <sub>0</sub> /[I] <sub>0</sub> <sup>a</sup>	Reaction time (h)	$M_n^{b}$ (g mol <sup>-1</sup> )					
			PF	PSA	$PDI^b$	$T_{\rm d}^{\ c}$ (°C)	$T_{\rm c}$ (°C)	$T_{\rm m}$ (°C)
PF <sub>7</sub> -Br	_	_	2610		1.61	_	_	
PF <sub>7</sub> -b-PSA <sub>64</sub>	150	48	2610	20810	1.63	383	37.2	44.4
PF <sub>7</sub> -b-PSA <sub>93</sub>	300	48	2610	30250	1.67	376	38.0	45.5
$PF_7$ -b-PSA <sub>166</sub>	500	48	2610	53920	1.88	367	38.7	46.1

measured by TGA under N<sub>2</sub>.

#### Preparation of microporous films

Block copolymers of PF-*b*-PSA were dissolved in chloroform solution with a fixed concentration of 5, 10, 30, or 50 mg ml<sup>-1</sup>. The polymer solution was cast on an untreated glass substrate in an adequate moist air flow hood at room temperature (30 °C).

# Characterization

All the composition, molecular weight, and PDI of synthesized polymers were determined by NMR and GPC. <sup>1</sup>H nuclear magnetic resonance (NMR) data was recorded at room temperature on a Bruker AV 500 MHz spectrometer using the residual proton resonance of the deuterated chloroform. Gel permeation chromatographic analysis was performed on a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD GmbH. All GPC analyses were performed on polymer/THF solution at the flow rate of 1 ml min<sup>-1</sup> at 40 °C and calibrated with polystyrene. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of 20 and 10 °C min<sup>-1</sup> using a TA instrument (TGA-951 and DSC-910S), respectively. UV-visible absorption and PL spectra of the copolymer solutions were recorded by a UV-visible spectrophotometer (Jasco V-570) and Fluorolog-3 spectrofluorometer (Jobin Yvon), respectively.

The morphologies of microporous films were investigated through a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6330F). SEM samples were sputtered with platinum prior to the images characterization and analysis was operated at an acceleration of 5 kV. Fluorescence optical microscope images were taken using Two Photon Laser Confocal Microscope (Leica LCS SP2). The polymer structure was further investigated by transmission-mode wide angle X-ray scattering (WAXS) at beam line 17A of National Synchrotron Radiation Research Center, Taiwan. The contact angles of water droplets to the microporous films were measured with an optical contact angle meter (CAM-100, Creating Nano Technologies Inc., Taiwan) at room temperature.

# 3. Results and discussion

#### Synthesis and characterization of rod-coil block copolymers

<sup>1</sup>H-NMR spectra and GPC were used to confirm the successful synthesis of the copolymer PF-*b*-PSA. Fig. 1 shows the <sup>1</sup>H NMR

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spectrum of PF7-b-PSA166 in CDCl3. The proton signals of the long alkyl chain and oxymethylene on PSA are clearly observed in the regions of 0.86-0.90, 1.21-1.34, 1.59-1.65 and 3.99-4.13 ppm, implying the successful incorporation of the PSA. The weak signals between 7.25-7.84 ppm are attributed to the protons on aromatic fluorene and phenyl end group, as compared to those of the PF-Br macroinitiator, as shown in Fig. S1(a). Note that PF7-b-PSA166 has a much longer PSA chain length than that of PF and thus weak signals of the fluorene proton resonances are observed. Also, the smaller peak d than that of peak e in Fig. 1 is probably the split resulting from the tacticity of the methylene group.<sup>31</sup> The <sup>1</sup>H NMR of the other two PF-b-PSA (PF7-b-PSA64 and PF7-b-PSA93) are shown in Fig. S1 (b) and S1(c), which are also consistent with the proposed structures. The GPC profiles of the block copolymers shift to the high molecular weight regions with enhancing the feed ratio, as shown in Fig. S2 of the Supporting Information. The  $M_n$  of these PF-b-PSA copolymers are 23417, 32860, and 56530, respectively, with corresponding PDI values of 1.63, 1.67, and 1.88, as listed in Table 1. The estimated SA repeating units of three copolymers from  $M_{\rm p}$  are 64, 93, and 166, and thus denoted as PF<sub>7</sub>-b-PSA<sub>64</sub>, PF7-b-PSA93, and PF7-b-PSA166, respectively. Chloroform, THF, and chlorobenzene are common solvents for both blocks of the copolymers.

Fig. 2 shows the DSC curve of  $PF_{7}$ -*b*-PSA<sub>166</sub> while the thermal decomposition curve is exhibited in the inset figure. As listed in Table 1, the  $T_d$  (at 5% sample decomposition) of PF-*b*-PSA are



Fig. 1 <sup>1</sup>H NMR spectrum of PF<sub>7</sub>-*b*-PSA<sub>166</sub> in CDCl<sub>3</sub>.



**Fig. 2** The DSC thermogram of  $PF_{7}$ -*b*-PSA<sub>166</sub> at a heating rate of 20 °C min<sup>-1</sup> under a nitrogen atmosphere. The inset shows thermal decomposition temperature at a heating rate of 20 °C min<sup>-1</sup> under a nitrogen atmosphere.

between 367 and 383 °C (Fig. S3 of the *Supporting Information*), which are reduced by increasing the PSA block length. On the other hand, the melting temperature  $(T_m)$  and crystallization temperature  $(T_c)$  are slightly increased with a higher PSA block length, which are 44.4–46.1 °C and 37.2–38.7 °C, respectively (Fig. S4 of the *Supporting Information*). Also, the  $T_m$  and  $T_c$  are higher than the PSA homopolymer  $(T_m = 37.2 \text{ °C}, T_c = 30.1 \text{ °C})$  due to the different coil length of PSA and the introduction of the rigid PF segment.

Fig. 3(a) shows the optical absorption and photoluminescence (PL) spectra of the PF-*b*-PSA, respectively. The absorption maximum wavelengths ( $\lambda_{max}^{abs}$ ) of PF-*b*-PSA in chloroform solution and thin film are observed at 370 and 376 nm, respectively, attributed to the  $\pi$ - $\pi^*$  transition of the PF block. Although there is no difference on the  $\lambda_{max}^{abs}$ , the absorption band becomes narrower with increasing the PSA block length. The emission maximum wavelengths ( $\lambda_{max}^{PL}$ ) of the PF<sub>7</sub>-*b*-PSA<sub>64</sub>, PF<sub>7</sub>-*b*-PSA<sub>93</sub>, and PF<sub>7</sub>-*b*-PSA<sub>166</sub> thin films are observed at (423, 445), (419, 442), and (413, 436) nm, respectively. The narrower absorption band and the blue shifting on the emission band suggest the reduced PF aggregation with increasing the PSA block length in PF-*b*-PSA.

#### The morphologies of microporous films

Fig. 4 shows the mechanism of forming highly ordered microporous films *via* crystalline conjugated rod–coil block copolymers, PF-*b*-PSA. PF-*b*-PSA was dissolved in chloroform (CHCl<sub>3</sub>) first and then cast on an untreated glass substrate in an adequate moist air flow hood at room temperature (30 °C) under the relative humidity of 65–90%. In the following, the surface temperature was cooled to a low temperature of -6 to 0 °C during the evaporation of CHCl<sub>3</sub>. When air containing moisture came into contact with the surface of polymer solution, moisture condensed to form water droplets on the surface. Note that the contact angles of PF and PSA are around 95° and 115°, respectively. The polymer phase would be composed of the top layer (conjugated PF block) close to the water drop and the bottom layer (crystalline PSA). After a few minutes, regular



**Fig. 3** UV-vis absorption and photoluminescent spectra of the studied PF-*b*-PSA copolymers: (a) in chloroform solution and (b) spin-coated thin films.

bubble arrays formed on the surface of the drop-cast film, which was white and opaque in appearance. Then, the regular threedimensional (3D) rod-*co*-valley-like film formed after removing the superhydrophobic top layer.

The structure of the microporous films were investigated by SEM, fluorescence microscopy, and WAXS. The samples for the SEM images (Fig. 5(a)-5(d)) of PF7-Br, PF7-b-PSA64, PF7-b-PSA93, and PF7-b-PSA166 microporous films were prepared from the concentration of 10 mg ml<sup>-1</sup> in CHCl<sub>3</sub> at the relative humidity of 65%. As shown in Fig. 5(a), the SEM image of PF<sub>7</sub>-Br macroinitiator film is irregular and broken, due to its low molecular weight. However, the microporous structures of PF7b-PSA<sub>64</sub>, PF<sub>7</sub>-b-PSA<sub>93</sub>, and PF<sub>7</sub>-b-PSA<sub>166</sub> have the average diameters of  $0.44 \pm 0.19 \,\mu\text{m}$  (coefficient of variation (CV) = 43%, the CV is a normalized dispersion of a probability distribution),  $0.87 \pm 0.32 \ \mu m \ (CV = 36\%), \ and \ 1.78 \pm 0.13 \ \mu m \ (CV = 8\%),$ respectively. Note that the average pore diameter is estimated based on a statistical average of over two hundred pores on each sample. The average pore size is increased with enhancing the PSA block length because the higher molecular weight leads to a slower rate of precipitation.32 Uniform microporous film of  $PF_7$ -b-PSA<sub>166</sub>, is obtained over the area of 0.3 cm<sup>2</sup>, which has the lower CV value of 8% and without an "island region" flat area. It suggests the comb-like compact structure of the PSA block with a long alkyl side chain could facilitate the stabilization of the water droplets and result in an ordered microporous structure.





Fig. 4 Proposed mechanism for the formation of the highly ordered microporous film from the crystalline conjugated rod-coil polymers of PF-b-PSA.

The ordering of the porous structure could be further improved by changing the solution concentration or humidity, as discussed in the following section.

The effect of alkyl side chain on the formation of microporous films was further investigated using  $PF_{7}$ -*b*-PMMA<sub>810</sub> with an amorphous coil for comparison. In a sharp contrast, the surface structure in the  $PF_{7}$ -*b*-PMMA<sub>810</sub> film (Fig. 5(e)) is composed of 50% pores and 50% flat regions while the pores are irregular in distribution of size. From the literature,<sup>32</sup> the film cast from pure linear PMMA did not form the microporous structure. It indicates the significance of using crystalline comb-like PSA coil in conjugated rod–coil block copolymers for fabricating ordered microporous films.

Next, the variation of processing conditions, such as polymer solution concentration and humidity, was used to obtain highly ordered bubble array structures of  $PF_{7}$ -*b*-PSA<sub>166</sub> microporous films. Fig. 6(a)–6(d) shows the SEM images of  $PF_{7}$ -*b*-PSA<sub>166</sub> microporous film prepared from different concentrations of 5, 10, 30, and 50 mg ml<sup>-1</sup> in CHCl<sub>3</sub> at a high relative humidity of 90%. As exhibited in Fig. 6(a), small and irregular pores formed and dispersed on the surface, since the low polymer concentration was not enough to encapsulate the condensed water drop. As the concentration increased to 10 mg ml<sup>-1</sup> (Fig. 6(b)), bubble arrays and some bigger pores were formed on the polymer

surface, which are the imprint of coalescence between unstable droplets during water condensation process. As the concentration increased further to 30 (Fig. 6(c)) and 50 (Fig. 6(d)) mg ml<sup>-1</sup>, the bubble arrays with highly ordered porous structures with pore diameters of 2.33  $\pm$  0.096  $\mu$ m (CV = 4.13%) and 1.85  $\pm$  $0.076 \,\mu m \,(\text{CV} = 4.10\%)$ , respectively, were formed. As expected, the pore diameter is smaller at a high concentration but with a higher pore density in Fig. 6. Compared to the low concentration of 10 mg ml<sup>-1</sup>, the higher concentration of 50 mg ml<sup>-1</sup> increases the polymer density and solution viscosity. Thus, the precipitation rate would be enhanced,33 stabilize water droplets and inhibit water from aggregating to form interconnected holes. The pores shown in Fig. 6(d) are nearly monodisperse and defectfree over large scale around 0.5 cm<sup>2</sup>. In addition, the enlarged SEM image (Fig. S6 of the Supporting Information) exhibits that the each pore is surrounded by six pores and the distance of center-to-center between pores is  $4.52 \pm 0.15 \ \mu m \ (CV = 3.3\%)$ . The relatively small coefficient of variation suggests the similar distance of any two neighbor pores.

Generally, bubble arrays do not form in a surrounding that has less than 45–50% relative humidity or without moisture flow during the casting process.<sup>6</sup> However, the SEM images of PF<sub>7</sub>-*b*-PSA<sub>166</sub> show the average pore size of  $1.30 \pm 0.22 \ \mu m$  (CV = 16%),  $1.56 \pm 0.16 \ \mu m$  (CV = 10%), and  $1.85 \pm 0.076 \ \mu m$ 



**Fig. 5** Top view of SEM images of drop-casting film prepared from the concentration of 10 mg ml<sup>-1</sup> at the relative humidity of 65%: (a) PF–Br, (b) PF<sub>7</sub>-*b*-PSA<sub>64</sub>, (c) PF<sub>7</sub>-*b*-PSA<sub>93</sub>, (d) PF<sub>7</sub>-*b*-PSA<sub>166</sub>, and (e) PF<sub>7</sub>-*b*-PMMA<sub>810</sub>.



Fig. 6 SEM images of  $PF_7$ -*b*-PSA<sub>166</sub> bubble arrays formed by evaporation of chloroform as concentration varied from 5 mg ml<sup>-1</sup> to 50 mg ml<sup>-1</sup> at the relative humidity of 90%: (a) 5 mg ml<sup>-1</sup>, (b) 10 mg ml<sup>-1</sup>, (c) 30 mg ml<sup>-1</sup>, and (d) 50 mg ml<sup>-1</sup>.

(CV = 4.1%) prepared at humidity (65%, 75%, and 90%) at the same concentration (50 mg ml<sup>-1</sup>) in Fig. 7(a)–7(c). The pore size was obviously increased at a higher humidity due to the enhanced amount of moisture contained in the air, similar to the literature.<sup>34</sup> Besides, the regularity of pores was enhanced at



Fig. 7 The SEM images of  $PF_{7}$ -*b*-PSA<sub>166</sub> drop-casting film prepared from the concentration of 50 mg ml<sup>-1</sup> at the relative humidity of (a) 65%, (b) 75%, and (c) 90%.

the higher relative humidity condition. In addition, the area of bubble arrays at 90% relative humidity is higher than those of others, indicating the possibility of constructing highly ordered microporous structure. The laser confocal microscope images of the  $PF_{7}$ -*b*-PSA<sub>166</sub> microporous film (Fig. 8) show the highly ordered microporous structure with a strong and uniform blue emission contributed by the conjugated PF rod block.

In order to investigate the interior morphology of the bubble arrays under a highly ordered  $PF_{7}$ -*b*-PSA<sub>166</sub> microporous surface, the sample was packed into a flask containing liquid nitrogen to solidify it instantly for a few minutes and then cut off the film immediately. Next, the film was quenched to room temperature under a surrounding vacuum until no residual water remained. After coating with platinum on the surface, the film



**Fig. 8** Laser confocal fluorescence microscopy images of  $PF_7$ -*b*- $PSA_{166}$  bubble arrays formed by the evaporation of chloroform in the microporous film. The inset figure shows the enlarged image of the studied film.

was characterized by SEM with a different tilted angle. As shown in Fig. 9(a) (SEM image, tilt angle 45°), the cross section of microporous film has a pore depth of 3  $\mu$ m and an underneath diameter of 4  $\mu$ m, which is larger than the open diameter (1.85  $\mu$ m) of the pore in the top-surface. It suggests an "egg



**Fig. 9** (a) FE-SEM image of cross-section structure of  $PF_7$ -*b*-PSA<sub>166</sub> order bubble array film tilted at 45° at the concentration of 50 mg ml<sup>-1</sup> at the relative humidity of 90%. (b) 3D reconstruction image *via* scanning laser confocal microscopy of  $PF_7$ -*b*-PSA<sub>166</sub> microporous film.

shape" water droplet sank into the polymer surface before further evaporation. The precipitating PF7-b-PSA166 layer is pulled around the water droplet by the high surface tension of the water, creating an egg shape cavity, and a smaller pore opening at the film surface.<sup>14</sup> Besides, a monolayer of bubble arrays is formed, resulting from the higher density of chloroform solvent than that of water. The microporous film thickness is around 7 um and the wall thickness existed between pores is around 200 nm. Each pore is independent and separated by a polymeric wall. From the cross-sectional SEM image, it shows the water leaves an imprint as bubble arrays in the microporous film. All bubbles arrays are independent and have equal shapes with regards to both the surface and interior morphologies. The threedimensional (3D) reconstruction of PF7-b-PSA166 microporous film via scanning laser confocal microscopy of bubble arrays (Fig. 9(b)) also shows that the monolayer and independent pores with highly ordered arrays are fabricated.

The ordering structure of the PF<sub>7</sub>-*b*-PSA<sub>166</sub> microporous film could be further evidenced by XRD. As shown in the synchrotron XRD analysis of Fig. 10, a sharp peak is observed at q =1.5 (A<sup>-1</sup>) (*d*-spacing = 0.41 nm), which is attributed to the PSA block (the inset figure). It indicates that the octadecyl alkyl side chains of PSA spontaneously arranged in ordered and crystalline structure without further annealing treatment. On the other hand, the wide angle X-ray scattering (WAXS) of PF<sub>7</sub>-*b*-PMMA<sub>810</sub> porous film shows the amorphous halo (Fig. S7 of the *Supporting Information*), but that of PF<sub>7</sub>-*b*-PSA<sub>166</sub> reveals an obvious sharp crystal peak.

# Fabrication of superhydrophobic property by the peeling off process

The top layer of  $PF_{7}$ -*b*- $PSA_{166}$  micorporous films was peeled off by adhesive tape to form a highly ordered rod-*co*-valley-like structure, as shown in Fig. 11. Note that the lotus effect exhibits superhydrophobicity due to the low surface energy and rough three-dimensional surface structure (hills and valleys).<sup>27,35,36</sup> From the top view image of SEM (Fig. 11(a)), the pore diameter (4 µm) is much bigger than that (1.85 µm) before peeling



**Fig. 10** Synchrotron XRD profiles of the PF<sub>7</sub>-*b*-PSA<sub>166</sub> microporous film. The inset shows the XRD profile of PSA film.



**Fig. 11** The images of  $PF_7$ -*b*-PSA<sub>166</sub> microporous film after peeling off the skin layer: (a) top view SEM, (b) cross-section SEM tilted at 45°, and (c) 3D reconstruction image *via* scanning confocal laser microscopy. The insets of (b) and (c) show the resulted superhydrophobicity (contact angle > 160°) and the water-adhesion ability for the prepared film, respectively.

(Fig. 7(c)). The surface structure exhibits a highly ordered rodco-valley-like structure in cross-section SEM image (Fig. 11(b)), and the length and thickness of these rods are around 2  $\mu$ m and 200 nm (Fig. S8 of the *Supporting Information*), respectively. Such a rougher micro-structure could enhance the superhydrophobicity and raise the contact angle from  $130 \pm 0.5^{\circ}$  up to  $163 \pm 0.3^{\circ}$  due to the lotus effect (the inset image of Fig. 11(b)). In addition, uniform blue-emitting from the 3D reconstruction *via* scanning laser confocal microscopy is also observed in Fig. 11 (c). In general, the water droplet should slide or roll off spontaneously on such superhydrophobic structure surface in a spherical form. However, it did not matter which angle between 0° to 180° the film was tilted from, the rolling of water droplet was inhibited (the inset image of Fig. 11(c)). The water-adhesion ability is probably resulted from the interaction of van der Waals force or hydrogen bonding<sup>35,36</sup> between water molecules and C= O groups of PF-*b*-PSA. The above results suggest that the highly ordered rod-*co*-valley-like<sup>36</sup> materials with both superhydrophobic and luminescent characteristics could be successfully prepared crystalline conjugated rod-coil copolymers.<sup>37</sup>

# 4. Conclusions

In summary, we have successfully fabricated novel luminescent and highly ordered microporous film from crystalline conjugated rod–coil diblock copolymers of PF-*b*-PSA. Compared to amorphous linear coil block, crystalline comb-like PSA coil blocks effectively form the highly ordered microporous film through the BF process due to their long alkyl side chain. The ordering of the pore structure was enhanced by the PF-*b*-PSA with a longer PSA block length, higher polymer solution concentration or humidity. Furthermore, a rod-*co*-valley-like superhydrophobic surface with a contact angle of  $163 \pm 0.3^{\circ}$  was achieved when the skin layer of the ordered microporous surface was peeled off. The above results suggest the highly ordered rod-*co*-valley-like materials with both superhydrophobic and luminescent characteristics could be prepared by new crystalline conjugated rod–coil copolymers.

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