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Bicontinuous Network Nanostructure with Tunable Thickness Formed on Asymmetric Triblock Terpolymer Thick Films

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Supporting Information

ABSTRACT: Asymmetric poly(1,1-dimethyl silacyclobutane)-*block*-polystyrene-*block*-poly(2-vinyl pyridine) (PDMSB-*b*-PS-*b*-P2VP) thick films, consisting of a spongelike substructure topped by a nanostructured dense top layer, were produced by combining a fast self-assembly of the triblock terpolymer chains with nonsolvent-induced phase separation (referred as SNIPS). A controlled evolution of the thickness and morphology of the nanostructured top layer was achieved upon solvent vapor annealing (SVA). For instance, the sub-100 nm thick square array morphology generated by SNIPS is transformed into a 1.5 μm thick core-shell perforated lamellar (PL) structure when exposed to a chloroform (CHCl_3) vapor for 3 h. A PL phase having highly ordered continuous P2VP nanochannels can be envisioned as an appealing morphology for membrane applications, since such a network structure formed on asymmetric PDMSB-*b*-PS-*b*-P2VP thick films obviates the need for alignment. Monoliths entirely composed of the bicontinuous PL structure were also produced by increasing the duration of the SVA treatment (18 h, CHCl_3).

In many challenging separations, polymeric membranes are favored over other processes, since such kind of materials afford energy efficiency, manufacturing scalability, low cost, and ease of handling.¹ However, conventional membrane-based separations innately bear a permeability–selectivity trade-off² and are subject to practical challenges such as fouling, degradation, and material failure that limit their use over time.³ To address the former issue facing separations, it is essential to make progress toward the large-scale fabrication of innovative materials having a high areal density of pores with well-controlled sizes to produce membranes that combine high selectivity with high flux for applications beyond simple filtrations.

The formation of isoporous membranes, generated by combining the self-assembly of block copolymers (BCPs) with nonsolvent-induced phase separation (SNIPS), is a promising route to tackle this challenge. In particular, asymmetric membranes with uniform pore sizes in high areal density have been demonstrated via this methodology both for AB- and ABC-type BCPs,^{4,5} where the benefits of moving from diblock copolymers to triblock terpolymers were clearly established in terms of enhanced mechanical properties of the membrane. In addition, ABC-type BCPs offer a unique opportunity to fabricate membranes with a panoply of network structures^{6–11} that could be used as innovative platform for the

nanodesign of next-generation membranes,^{12,13} thereby potentially opening a large set of practically important separations. For instance, ABC-type network morphologies such as the core-shell double-gyroid (G, space group: $Ia\bar{3}d$) and diamond (D, $Pn\bar{3}m$) structures, their alternating versions (G^A , $I4_132$ and D^A , $Fd\bar{3}m$), or even the $Fddd$ (O^7) and perforated lamellar (PL, $P6_3/mmc$ or $R\bar{3}m$) phases would be relevant candidates for challenging separation applications. Indeed, these interconnected morphologies bring stability to the (bio)molecule transport through the channels with respect to all sorts of structural defects and obviate the need for alignment.

To further advance the implementation of this emerging technology, new insights into the structure formation within the membrane skin layer have to be gained, since reproducible manufacturing on a large scale constitutes a bottleneck for the development of such high-performance materials.^{14,15} So far, the SNIPS process usually leads to the formation of a kinetically trapped low-dimensional nanostructure, making still uncertain the manufacture of highly selective and defect-free

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Figure 1. Top-view SEM images of asymmetric DSV-51k/DSV-43k thick films ($t \sim 19 \mu\text{m}$) generated by SNIPS and then exposed to a CHCl_3 vapor for different times: (A, B) 0 h, (C, D) 0.5 h, and (E, F) 3 h. The DSV-51k thick films blended with 25 wt % DSV-43k were immersed into an aqueous solution of HAuCl_4 and subsequently treated by CF_4/O_2 RIE plasma to distinguish the HAuCl_4 -stained P2VP (bright) and superficially etched PDMSB (dark) domains from the PS (gray) phase. The upper and lower panels show the nanostructures and substructures, respectively, of the DSV-51k/DSV-43k thick films in the vicinity of the top free surface. (Inset) Schematic representation of a bicontinuous PL structure with HAuCl_4 -stained P2VP (yellow)/PS (blue) core-shell perforations. Scale bars: 200 nm.

membranes in reproducible fashion for challenging applications (e.g., separation of similar-sized molecules such as proteins).³

To maintain adequate transport of molecules and high selectivity of the membrane, the formation of long-range ordered network structures on the top surface is envisioned as an alternative route to alleviate the need for a defect-free cylindrical array.¹⁶ For this purpose, a methodology driving the microphase separation of BCP membranes toward a network structure is required. To achieve well-ordered three-dimensional (3D) morphologies and control the growth of the network structure at the expense of the macroporous substructure, the solvent vapor annealing (SVA) approach is an effective methodology, since SVA has been successfully introduced in BCP nanotechnologies to produce thin film complex nanoscale patterns (e.g., alternating or core-shell “three-color” patterns,^{17–22} and Archimedean tilings^{23–26}), which are unattainable through thermal annealing. As SVA is a powerful technique to achieve long-range ordered nanostructures, no efforts are required to preorder the BCP chains on the membrane skin layer, which can be viewed as the Achilles heel of the SNIPS process. Herein, we highlight a simple and scalable technique to improve the long-range order of the nanophase formed on the dense top layer of a macroporous asymmetric structure. Particularly, a combination of SNIPS and SVA is used to produce a long-range ordered perforated

layered (PL) structure on the top surface of asymmetric triblock terpolymer thick films. Tunability of the dense top layer thickness from few hundred nanometers to several micrometers is achieved by varying the SVA time. Such a control of the skin layer thickness could potentially contribute to higher permeability–selectivity combinations. PL-structured monoliths are also demonstrated for specific SNIPS–SVA treatments.

RESULTS

Fabrication of Asymmetric and Nanoporous Thick Films by SNIPS. The two original linear ABC triblock terpolymers, poly(1,1-dimethyl silacyclobutane)-*block*-polystyrene-*block*-poly(2-vinyl pyridine) (or PDMSB-*b*-PS-*b*-P2VP, noted hereafter DSV) used in this work, were prepared by sequential anionic polymerization to achieve narrow dispersities, $\bar{D}$. These PDMSB-*b*-PS-*b*-P2VP terpolymers have molecular weights, M_n , of 43 kg mol^{−1} ($\bar{D} < 1.1$) and 51 kg mol^{−1} ($\bar{D} < 1.2$) and different compositions ($\text{D/S/V} = 15:65:20$ for DSV-43k and $\text{D/S/V} = 32:36:32$ for DSV-51k). The small-angle X-ray scattering (SAXS) pattern of a thermally annealed (180 °C, 24 h) DSV-51k bulk sample showed a first-order peak, q^* , at 0.141 nm^{−1} and higher-order peaks located at $q/q^* = 1, 2, 3, 4, 5, 7$, and 8, consistent with a lamellar phase having a period of ~ 44.5 nm (see Figure S1). Conversely, the SAXS pattern of the thermally annealed (180 °C, 24 h) DSV-

Figure 2. Cross-sectional view SEM images of a solvent-annealed (3 h, CHCl_3) DSV-51k/DSV-43k thick film ($t \sim 19 \mu\text{m}$) generated by SNIPS–SVA showing (A) the full-graded thick film on a Si substrate, (B) the PL nanostructure located on the film free surface, and (C) the macrostructure in contact with the substrate. (D) Top-view SEM image of a DSV-51k thick film blended with 25 wt % DSV-43k showing a $1.5 \mu\text{m}$ thick PL structure formed on a dense spongelike substructure.

43k bulk sample was indexed to an alternating cylindrical phase ordered into a tetragonal array having a period of $\sim 27 \text{ nm}$ ($q^* = 0.22 \text{ nm}^{-1}$) (see Figure S1). The higher-order peaks located at $q/q^* = 1, 2^{1/2}, 5^{1/2}$, and $13^{1/2}$ correspond to the (10), (11), (21), and (32) diffraction planes, respectively, of the square lattice. Such results are consistent with Mogi et al.'s report²⁷ on the phase behavior of a polyisoprene-*b*-PS-*b*-P2VP (ISV) series along the $\phi_1 \approx \phi_V$ isopleth (where ϕ_A is the composition of the A block). Indeed, the lamellar and alternating cylindrical phases were observed for similar ranges of compositions (I/S/V = 36:31:33 for lamellae and I/S/V = 14:68:18 for cylinders). Based on Mogi et al.'s study,²⁷ all DSV-51k thick films, presented in this work, were blended with 25 wt % DSV-43k terpolymer (D/S/V = 28:43:29 for the blend) to reach a range of compositions over which a network morphology was formed (I/S/V = 26:48:26). The blended DSV-51k/DSV-43k bulk sample, prepared by solvent casting (CHCl_3) and subsequent thermal annealing (180°C , 24 h), confirmed the formation of a network structure, since the SAXS pattern revealed a series of Bragg peaks, located at $q/q^* = 1, 3^{1/2}, 7^{1/2}, 4$, and 5 ($q^* = 0.16 \text{ nm}^{-1}$), indicative of a hexagonally perforated layer (HPL) which coexists with a lamellar phase (see Figure S1). Here, the SAXS peaks, at $q/q^* = 1, 3^{1/2}$, and $7^{1/2}$, were assigned to a HPL phase, since other hexagonal structures such as the core-shell cylindrical and cylinder-in-lamellar phases are not expected for this range of compositions.

Blended DSV thick films were drawn into a silicon substrate from a 18 wt % terpolymer solution in a mixture of 1,4-dioxane and tetrahydrofuran (DOX/THF: 80:20 by weight) using a doctor's blade set at a gate height of $225 \mu\text{m}$. After the polymer layer was cast, the solvent was allowed to evaporate for 30 s, during which the concentration of the polymer at the air/film interface increased to form a nanoporous skin layer. Importantly, the polymer layer was allowed to evaporate for 30 s because shorter-duration processes do not generate a homogeneous dense skin layer (e.g., sporadic macropores were observed) as reported previously,⁵ while longer-duration processes do not necessarily improve the long-range order of the nanostructure. The polymer layer was subsequently immersed in an appropriate nonsolvent (water) bath (i.e.,

miscible with the DOX/THF mixture) to induce the formation of the macroporous substructure.

Scanning electronic microscopy (SEM) images presented in Figures 1A,B and S2 show the resulted macroporous and nanoporous structures generated by SNIPS. Dynamic light scattering (DLS) showed unimers in a solution with a hydrodynamic diameter (D_h) of 8 nm and the presence of two micelle populations ($D_h = 48$ and 457 nm) (see Figure S3a), while the resulted spongelike substructure consisted of densely packed micelles having a narrow diameter distribution centered at approximately 30 nm in the dried form (see Figure S3b). These results suggest that the micellar objects with a mean diameter of 48 nm have a tendency to aggregate into larger objects in a solution. Note that the more hydrophobic block (i.e., PDMSB), forming the core of micelles to avoid contact with the hydrophilic ether solvents, clearly appears in black in the SEM images, while the PS (gray) shell cannot be distinguished from a possible P2VP corona (surface energy: $\gamma_{\text{PDMSB}} = 27.3 \text{ mN m}^{-1}$,²⁸ $\gamma_{\text{PS}} = 43.5 \text{ mN m}^{-1}$,²⁸ $\gamma_{\text{P2VP}} = 50 \text{ mN m}^{-1}$ ²⁹). To get an insight on the morphology produced by the self-assembled DSV terpolymers on the dense skin layer, the material was immersed in an aqueous HAuCl_4 solution and then subsequently treated by a low-energy CF_4/O_2 reactive ion etching (RIE) plasma to enhance the SEM contrast within the three-color pattern without creating any additional spanning of the pores across the dense top surface layer (i.e., voided PDMSB nanodomains are not generated).³⁰ Such a soft treatment reveals that the HAuCl_4 -stained P2VP (bright) and superficially etched PDMSB (dark) domains form an alternating structure arranged in a short-range ordered square array having a period of $\sim 29 \text{ nm}$ (see also Figure S4). It is noteworthy that this kinetically trapped morphology differs from the bulk morphology.

Improving the Long-Range Order of the Nanostructure by SVA. To produce long-range ordered nanostructures, blended DSV thick films were exposed to a post-SVA process for different times in chloroform (CHCl_3). A stream of such a solvent was chosen to self-assemble the top layer of the asymmetric thick films because the highly ordered network structures formed by solvent-annealed (CHCl_3) DSV thin films have been demonstrated.³⁰ SEM images presented in

Figure 1C,D show a solvent-annealed (0.5 h, CHCl_3) DSV thick film. During the short SVA treatment ($t = 0.5$ h), the alternating morphology is transformed into another short-range ordered structure having a period of ~ 40 nm (see Figures 1C and S5). This PL structure, given in the inset of Figure 1D, consists of a P2VP-rich phase enclosed in PS lamellae and PDMSB lamellae perforated by P2VP/PS core-shell domains arranged into a pseudohexagonal array (see also Figure S6). Importantly, although a complete fusion of micelles is observed during the SVA process, the macroporous spongelike morphology is disrupted (i.e., the macropores did not get collapsed/filled during the SVA) (see Figures 1D and S7). Conversely, extremely long-range ordered P2VP/PS core-shell perforations can be observed from the solvent-annealed (3 h, CHCl_3) DSV thick films (see Figure 1E). For instance, the fast Fourier transform (FFT) of the atomic force microscopy (AFM) topographic image showing a single grain orientation over $3 \mu\text{m}^2$ of the PL (001) plane indicates that the P2VP/PS core-shell perforations are arranged into a highly ordered rhombic array ($c2mm$ crystallographic group) with the lattice parameters $a = 39.5$ nm and $b = 33.8$ nm (see Figure S8). Note that long SVA treatments also induce growth of the PL phase at the expense of the macroporous substructure as shown in Figure 1F. The corresponding grazing incidence small-angle X-ray scattering (GISAXS) pattern and its associated intensity cut along the in-plane q_y direction (computed around the Yoneda band) support this morphological assignment (see Figure S9). The $I(q_y)$ intensity profile, informative about the in-plane ordering, compares favorably with the FFT presented in Figure S8, and similar lattice parameters ($a = 39$ nm and $b = 33.1$ nm) were extracted from these data assuming the arrangement of the P2VP/PS core-shell perforations into a rhombic array.

To know more about this phenomenon, representative SEM images showing the lower and upper regions of the solvent-annealed (3 h, CHCl_3) DSV thick film are presented in Figure 2. Cross-sectional views show that the $19 \mu\text{m}$ thick DSV layer deposited on a silicon substrate displays an asymmetric structure that consists of a $1.5 \mu\text{m}$ thick PL morphology located on the dense top layer and a macroporous spongelike substructure in the vicinity of the substrate (see Figure 2A–C). In contrast, both the cross-sectional and top-view SEM images presented in Figure 2B,D reveal that the substructure region in contact with the PL structure is more compact, indicating that the macroporous phase densifies to form a disordered 3D morphology prior its transformation into a well-ordered network structure.

Structural Characterizations of the Network Structure. In general, the PL phase can order into a trigonal structure (space group: $R3m$) with an ABC stacking or a hexagonal structure (space group: $P6_3/mmc$) with an AB stacking.^{31,32} To further characterize the network structure formed on the top surface layer of the solvent-annealed (3 h, CHCl_3) DSV thick films, SEM images of the PL (100) and (101) patterns are displayed in Figure 3. The PL (100) pattern is useful to determinate the stacking sequence of perforations, since the alternating perforated layers are orthogonally oriented in the $[100]$ direction.³³ Here, the PDMSB (dark) phase projection reveals that the P2VP/PS perforations, extended through the PDMSB layers to form a bicontinuous structure, are arranged in an AB stacking (see Figures 3A and S10). These P2VP/PS core-shell perforations, stacked in the ABAB... sequence with a layer repeat distance, d_L , of 68 nm,

Figure 3. Top-view SEM images showing different plane orientations of the PL structure formed on the top free surface of the solvent-annealed (3 h, CHCl_3) DSV-51k/DSV-43k thick films ($t \sim 19 \mu\text{m}$) manufactured by SNIPS–SVA: Panels (A) and (B) correspond to the PL (100) and (101) planes, respectively. The upper and lower regions of (C) show undulated PDMSB and P2VP/PS lamellae along the (100) plane and the pseudohexagonal array formed by the P2VP/PS perforations extended through the PDMSB layers oriented along the $[100]$ direction. The HAuCl_4 -stained P2VP and superficially etched PDMSB domains appear in bright and dark, respectively, while the PS phase is in gray. Scale bars: 200 nm.

have an interdomain spacing, d_p , of 39.5 nm (see Figure S10). The ratio d_L/d_p equal to 1.72 is quite similar to that determined with accurate calculation for a HPL structure having an AB stacking ($d_L/d_p = 1.88$).³⁴ This is further supported by the GISAXS pattern (see Figure S9) in which the two first-order Debye–Scherrer rings corresponding to the transmitted and the reflected beams are split into a set of peaks having a distorted hexagonal symmetry, indicating a structure having a pseudohexagonal arrangement in the plane normal to the X-ray beam in accordance with the symmetry retrieved from Figure S9. The out-of-plane orientation of the P2VP/PS perforations is also retrieved on the two-dimensional (2D) GISAXS pattern with a set of Bragg rods strongly modulated in intensity along the q_z direction. A full indexation of the GISAXS pattern was performed using the GIXSGUI package,³⁵ and the diffraction peaks positions were best accounted on the basis of a $P6_3/mmc$ space group having the $[001]$ direction normal to the film surface, thus supporting the AB stacking. In contrast, an undulated lamellar morphology having a period of 39.5 nm can be observed along the (101) plane (see Figure 3B). Interestingly, the 2D-FFT corresponding to the AFM topographic image presented in Figure S11 indicates that the P2VP-containing modulations are well-distributed within the undulated PS lamellae, since the PL (101) pattern has a $c2mm$

Figure 4. Cross-sectional view SEM images of a solvent-annealed (18 h, CHCl_3) DSV-51k/DSV-43k monolith ($t \sim 19 \mu\text{m}$) generated by SNIPS–SVA showing the PL nanostructure (A) located on the material air surface, (B) in the vicinity of the Si substrate, and (C) within the material. (Inset) Top-view SEM image of a DSV-51k monolith blended with 25 wt % DSV-43k showing a highly ordered PL structure located in the middle of the mesoporous material. Scale bars: 500 nm.

symmetry (i.e., centered rectangular array with $a = 39.5$ nm and $b = 34.3$ nm). Intriguingly, the rhombic arrangement ($a = 39.5$ nm and $b = 33.8$ nm) of the PV2P perforations surrounded by a PS shell revealed to be locally stable over the common hexagonal or tetragonal packings expected for a perforated layer structure.³⁴ To support this observation, the lattice parameters a and b of the rhombic array along the [001] direction of the PL structure are well-retrieved within the different planes (i.e., $a_{(001)} = a_{(100)}$ and $b_{(001)} = b_{(101)}$). The SEM image presented in Figure 3C shows a region in the vicinity of the skin layer of a solvent-annealed (3 h, CHCl_3) DSV thick film from which the PL (101) and (100) planes can be clearly observed.

Fabrication of Monoliths Entirely Composed of a Network Structure. Monoliths entirely composed of a PL structure were also produced by increasing the duration of the SVA treatment. For instance, a PL-structured DSV material is achieved by exposing the film to CHCl_3 vapor for 18 h as evidenced by the presence of the network structure extended from the air surface of the monolith to the vicinity of the substrate (see Figure 4A,B). It is noteworthy that both the regions corresponding to the air surface and middle of the monolith exhibit a PL structure with a long-range orientational order, which can be locally maintained over $5 \mu\text{m}^2$ as shown in Figure 4C. In contrast, a characteristic “fingerprint” pattern can be observed close to the substrate, indicating that the orientational order parameter of the layered structure is decayed in this region of the monolith. This is because the macroporous phase must densify prior to transforming into a well-ordered PL structure, as already shown in Figure 2D.

DISCUSSION

SVA, in combination with SNIPS (SNIPS–SVA), has been used to demonstrate a highly ordered network structure with an adjustable thickness on the skin layer of asymmetric terpolymer thick films. This network structure is a PL phase consisting of rhombic packed P2VP/PS perforations extended through the PDMSB layers to form core–shell nanoscale

pathways. A continuous and permeable P2VP nanophase with controllable dimensions is highly desired for applications that require size-selective and/or charge-based separation of biomolecules.³⁶ Indeed, pyridine features a weakly basic lone pair of electrons that can be protonated under suitable pH conditions to tailor the membrane pore size (e.g., moving from ultrafiltration toward nanofiltration)³⁷ and/or to separate similar-sized biomolecules with different isoelectric points (e.g., proteins).³⁶

Tunability of the PL thickness from few hundred nanometers to several micrometers has been also demonstrated through the SVA duration. Such material property is very interesting to potentially optimize the interplay between the permeability and selectivity of the polymeric membrane, notably for medical processes like hemodialysis.³⁸ For instance, a macroporous substructure topped by a continuous network structure with a thickness corresponding to a single-layer perforation of the PL phase would constitute a membrane that combines high selectivity with maximized flux, which could substantially shorten the time spent by the patients for each day of hemodialysis treatment. However, an increase of the PL structure’s thickness would maximize the membrane selectivity. Indeed, a skin layer with a thickness equivalent to several unit cells would offer more stability over the structural defectivity by maintaining good size-cutoff properties through the tortuosity of the permeable pathways, which is required to ensure the health of the patients.

Monoliths with an internal continuous permeable network were also achieved for long SVA treatments. This kind of nanoporous network material becomes increasingly important for applications such as filtration chromatography, catalysis, and nanotemplating.³⁹ For example, such a 3D-network structure is an appealing morphology for photovoltaic applications,⁴⁰ since the preferable active layer design consisting of continuous semiconductor nanopathways can be achieved by using the PL-structured monolith as a template.

CONCLUSIONS

The growth of a bicontinuous network structure on asymmetric triblock terpolymer thick films has been achieved by using a simple and scalable methodology combining the SNIPS process with a SVA treatment. This highly ordered network structure having a tunable thickness demonstrates that the SNIPS–SVA process is an effective methodology to progress into manufacturing the next generation of membranes with unique properties. For instance, a high areal density of well-ordered continuous (permeable) nanopathways with perfectly defined dimensions on an asymmetric thick film is envisioned as an advanced architecture design to improve the reproducible manufacturing of self-assembled membranes, since the network structures avoid the need for alignment.

METHODS

Fabrication of Asymmetric DSV Thick Films. Nineteen microns thick DSV-51k/DSV-43k films were drawn onto (2×2 cm) silicon substrates by using a simple tape-casting technique from a 18 wt % terpolymer solution in a disolvent mixture (DOX/THF: 80:20 by weight). To produce asymmetric thick films, the solvents were allowed to evaporate during 30 s to form a dense air surface layer with a kinetically trapped nanoporous structure, and then the blended DSV material was immersed into a deionized water bath for 10 min to produce a macroporous substructure.

Self-Assembled Asymmetric Thick Films and Monoliths. The self-assembly of DSV terpolymers was promoted by exposing films for different times (ranging from 0 to 18 h) to a continuous stream of CHCl_3 vapor produced by bubbling nitrogen gas through the liquid solvent as described previously.⁴¹ This continuous flow system was used to control the CHCl_3 vapor pressure in the chamber by dilution with a separate N_2 stream so that a solvent vapor consisted of a 32 sccm CHCl_3 vapor and a 8 sccm N_2 (total 40 sccm). Importantly, the PL structure produced on the dense top layer during the early stage of the SVA treatment grows at the expense of the macroporous phase until the formation of a monolith entirely composed of the network structure.

SEM and AFM Characterizations. Scanning electron microscopy (SEM, JEOL 7800) was used in Gentle Beam mode (GBSH) at an accelerating voltage of 1 kV to acquire the DSV-51k/DSV-43k film images. Atomic force microscopy (AFM Dimension FastScan, Bruker) was used in the tapping mode to characterize the surface morphology of the blended DSV films. Silicon cantilevers (Fastscan-A) with a typical tip radius of ~ 5 nm were used. The resonance frequency of the cantilevers was about 1.25 kHz. Prior to SEM and AFM measurements, the blended DSV films were immersed into an aqueous HAuCl_4 solution (1 wt %, 2 h) and then subsequently etched with a fluorine-rich plasma treatment in PE-100 chamber (RIE, Plasma Etch) to partially remove the PDMSB phase (plasma conditions: 40 W, 17 sccm CF_4 , and 3 sccm O_2 , 180 mTorr, and 45 s).

Grazing Incidence Small-Angle X-Ray Scattering. GISAXS experiments were performed on the ALBA Synchrotron in Spain using a X-ray beam energy of 12.4 keV and a sample-to-detector distance of 3048 mm. The incidence angle was set at 0.1° , close to the critical angle of the thick film, to be highly sensitive to the film surface. 2D scattering patterns were collected using a PILATUS 1 M Dectris detector. GISAXS patterns were reduced using a home-made Matlab-based code. The intensity cuts along the horizontal q_y were extracted from the GISAXS patterns after normalization for the incident photons and the exposure time by averaging the intensity of five adjacent pixel arrays (corresponding to a $\Delta q = 0.01 \text{ nm}^{-1}$) along q_y where $q_y = 2\pi/\lambda[\sin(2\theta_f)\cos(\alpha_f)]$ and $q_z = 2\pi/\lambda[\sin(\alpha_f) + \sin(\alpha_i)]$ are the modulus of the scattering vectors in the directions parallel and perpendicular to the substrate plane, and α_i , $2\theta_f$, and α_f are the incident and scattering angles in the horizontal and vertical directions, respectively.

Small-Angle X-Ray Scattering (SAXS). SAXS experiments were performed on the D2AM French-CRG Beamline at the European

Synchrotron Radiation Facility (ESRF) in Grenoble, France. A XPAD 2D pixel detector was used for recording the 2D scattering images, and a 2400 mm sample-to-detector distance was chosen. The energy of the X-ray beam was 11 keV. The 2D images were radially averaged around the center of the primary beam to obtain the isotropic SAXS intensity profiles. The scattering pattern from a specimen of silver behenate was used for the calibration of the wavevector scale of the scattering curves. Finally, the data were normalized to the intensity of the incident beam to correct for primary beam intensity fluctuations.

Dynamic Light Scattering (DLS). DLS studies were conducted at 25°C using a Litesizer 500 Zetasizer Nanoseries instrument equipped with a 40 mW He–Ne laser operating at 658 nm. The samples were analyzed in quartz cuvettes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00572.

SAXS pattern profiles of the DSV-51k, DSV-43k, blended DSV-51k/DSV-43k samples; SEM images of the same region of a DSV-51k/DSV-43k thick film ($t \sim 19 \mu\text{m}$); particle size distribution obtained from DLS measurements for the DSV-51k/DSV-43k solution in DOX/THF; AFM topographic views of a DSV-51k/DSV-43k thick film ($t \sim 19 \mu\text{m}$) generated by SNIPS and a one then exposed to a CHCl_3 vapor during 30 min; schematic representation of a bicontinuous PL structure with HAuCl_4 -stained P2VP (yellow)/PS (blue) core–shell perforations; SEM image of a solvent-annealed (0.5 h, CHCl_3) DSV-51k/DSV-43k thick film; AFM topographic view and the 2D-FFT with its associated profile corresponding to the PL (001) plane of a solvent-annealed (3 h, CHCl_3) DSV-51k/DSV-43k thick film; 2D GISAXS pattern of a solvent-annealed (3 h, CHCl_3) DSV-51k/DSV-43k thick film ($t \sim 19 \mu\text{m}$) generated by SNIPS–SVA; SEM image of the PL (100) pattern; AFM topographic view and the 2D-FFT with its associated profile corresponding to the PL (101) plane of a solvent-annealed (3 h, CHCl_3) DSV-51k/DSV-43k thick film (PDF)

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Notes

The authors declare no competing financial interest.

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