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Stimuli Responsive Nanostructured Porous Network from Triblock Copolymer Self-assemblies

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ABA triblock amphiphilic copolymer is synthesized using RAFT chemistry. The self-assembled micelles of this copolymer are then used to prepare nano-organized porous films that could be used as filtration membranes. In this work a novel strategy is developed to build the nanostructures and perform their self-assembly using reversible and non-covalent interactions to create free volume between the micelles, thus giving tuneable porosity to the film. The self-assembly of poly(styrene)-*b*-poly(phenylboronic acid)-*b*-poly(styrene) block copolymer, occurs at high concentration through solvent evaporation, which induces a progressive decrease of the inter-micellar distance, and results in the formation of an in-situ network of micelles and the final porous film. Subsequent permeability tests were conducted under different stimuli (pH and UV), generating cross-linking and chemical exchange reactions, to ensure the best balance between permeability and mechanical strength. This work highlights an original strategy for pore size control, and provides new insights towards the design of stimuli-responsive materials.

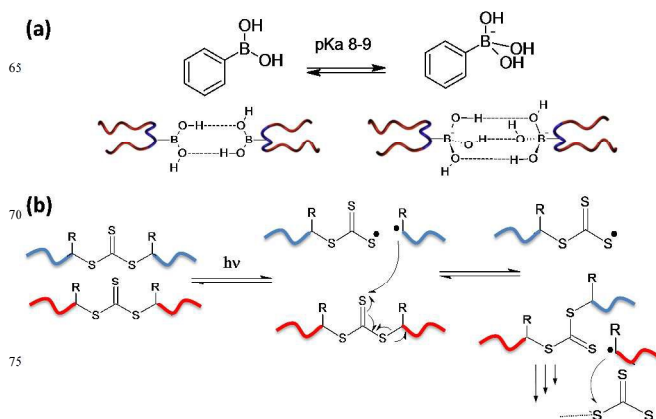
Introduction

The self-assembly of amphiphilic copolymer nanostructures into porous materials has attracted great interest in the past decade. Amphiphilic block copolymers are known for their self-assembly, which allows the fabrication of a variety of bottom up nanostructured materials [1-4]. Thermodynamic interactions between blocks are the main factor guiding the morphology, but these materials also have the possibility to form a range of structures in the kinetically trapped states [5]. Highly ordered nanostructure can be used in several applications such as ultrafiltration for water treatment [6], selective separation of solutes for pharmaceutical and food industry [7], drug delivery [8], medical filtration needs such as dialysis [9] and data storage [10].

Block copolymers offer great opportunities for the design of porous films with selective permeation through their regular structure. Previously, films have been fabricated from block copolymers using spin-coating, [7,11-13] extrusion, [14,15] and bulk evaporation [16-18] techniques, yet the porous films produced from these methods typically require post-fabrication modifications to convey porosity into the films and are not based on sturdy industrial processes. Recently the relevance of block copolymer micelle assembly in the fabrication of isoporous asymmetric membranes by solution casting and immersion in a non-solvent bath has been demonstrated [19-23]. This method does not require post-fabrication modifications and is based on the industry standard phase separation technique.

ABA-triblock copolymers (just like diblock copolymers) are good candidates for formation of networks. The design of such materials is dependent on the functionalities that could promote specific self-organization patterns or selective binding, to generate materials with controlled porosity and dynamic behavior. One example of such bindings is the specific

interactions between boronic acid groups. Below the pKa value of boronic acid (i.e. 8.9), hydrogen bonds are formed between water molecules and other boronic acid groups while at pHs above the pKa value, reversible boronate groups are formed (Scheme 1a). In addition, ABA triblock copolymers can self-assemble in 2 major configurations (flower and star) depending on the solvent system. In flower micelles the middle block is soluble while the outer block (A) is collapsed forming the core. In star micelles the middle block (B) is collapsed to form the core and the outer block (A) forms the micellar shell. In a flower configuration the polymeric chain could either form loops (with both "A" outer blocks forming the core of a single micelle) or bridges where the two ends of a single polymeric chain are shared between two adjacent micelles. The bridge configuration thus links micelles to one another and could help the formation of a porous network.



Scheme 1. Schematic representation of inter-micellar interactions; (a) Hydrogen bonding between phenylboronic acid groups below and above its pKa [24] (b) thiol exchange mechanism under UV irradiation [25].

In this paper we take a new approach to make organized mesoporous network from self-assembled amphiphilic copolymers. A poly(styrene)-*b*-poly(phenylboronic acid)-*b*-poly(styrene) triblock copolymer is synthesized using RAFT chemistry and self-assembled in a mixture of *N*-methyl-2-pyrrolidone (NMP) and water via microphase separation induced by a non-solvent (water) to form micelles. The resulting micelles are then assembled in form of a nano-organized film. The two interactions involved in the formation of the links between micelles are: 1) the supramolecular interactions of boronic acid present on the corona of micelles (Scheme 1a) and 2) the covalent bonds formed by the exchange of thiols (from the RAFT agent) induced by UV irradiation (Scheme 1b). These interactions are then modulated by varying the experimental conditions (pH and pressure) during filtration.

Experimental

Materials. All reagents were purchased from Sigma-Aldrich and were used as received unless otherwise stated. Azobisisobutyronitrile (AIBN) was purchased from Fluka Chemika and was recrystallized from methanol. 4-vinylphenylboronic acid (PBA) 97% was purchased from Alfa Aesar and was used as received. Styrene (St) was passed through basic alumina prior to use. Deuterated solvents were purchased from Eurisotop.

Synthesis of S,S'-bis-(α,α' -disubstituted- α'' -acetic acid)-trithiocarbonates (DTTC). This product was synthesized following the method described by Lai et al. [26]. Under inert atmosphere (N_2), 120 mL of mineral spirits was mixed with carbon disulfide (27.4 g, 0.36 mol), chloroform (107.5 g, 0.90 mol), acetone (52.3 g, 0.90 mol) and tetrabutylammonium bisulfate (2.41 g, 7.10 mmol) in a 1.0 L three neck round bottom flask. Sodium hydroxide (50%) (201.6 g, 2.52 mol) was added drop wise over 90 minutes keeping the temperature under 25 °C. The reaction was stirred overnight. The yellowish solid was then dissolved in 900 mL of distilled water, followed by 120 mL of concentrated HCl. The mixture was stirred for 30 min in a stream of nitrogen. The solid was collected and washed thoroughly with distilled water. The yellow product was recrystallized in acetone. 1H NMR (MeOD₄, ppm): 1.66 (CH₃), 4.84 (COOH).

Synthesis of the Polystyrene macro-chain transfer agent (PS macro-CTA). A round bottom flask was charged with styrene (25.0 g, 0.24 mol), DTTC (0.99 g, 3.5 mmol), 2,2'-azobisisobutyronitrile (AIBN; 29 mg, 0.17 mmol); DTTC/AIBN molar ratio = 20.0) and dimethylformamide (DMF) (2.0 mL for dissolution of DTTC). The sealed reaction vessel was purged with nitrogen and placed in a pre-heated oil bath at 70 °C for 5 days. The resulting PS (Styrene conversion = 58 %; M_n = 4,900 g mol⁻¹, M_w = 5,100 g mol⁻¹, \bar{D} = 1.03) was purified by precipitation into excess cold methanol and dried under vacuum (Fig. S1, 2, 5).

Synthesis of polystyrene-*b*-poly(4-vinylphenyl boronic acid)-*b*-polystyrene (PS-PPBA-PS) triblock copolymer. PBA (25.0 g; 0.054 mmol), AIBN (8.0 mg; 0.49 mmol), PS macro-CTA (4.8 g; 1.0 mmol; macro-CTA/initiator molar ratio = 2.0) were dissolved in DMF (15.0 mL). The reaction mixture was sealed in a round-bottomed flask and purged with nitrogen gas and placed in a pre-heated oil bath at 70 °C for 5 days (final PBA conversion = 58 %; M_n = 10,310 g mol⁻¹, M_w = 11,600 g mol⁻¹, \bar{D} = 1.12). The resulting triblock was purified by precipitation into excess cold ethanol and dried under vacuum (Fig. S3, 4, 5).

Triblock self-assembly. The self-assembled solution of the triblock copolymer was prepared as follows; 2 mg of the triblock copolymer was dissolved in 1.0 mL *N*-methyl-2-pyrrolidone (NMP). The solution was stirred overnight at room temperature. Upon complete dissolution 1.0 mL of distilled water was added drop wise to obtain the micellar solution. The dynamic light scattering measurement suggests a hydrodynamic diameter of 215 nm (stable over several days).

Film preparation. A circular disc of cleaned non-woven polyester tissue was first filled/ wetted with chloroform and then the micellar solution is deposited on the surface of the support using a tape casting knife at 250 μ m. This film is then kept under humid atmosphere (70% humidity) for 24h prior to immersing in a water coagulation bath.

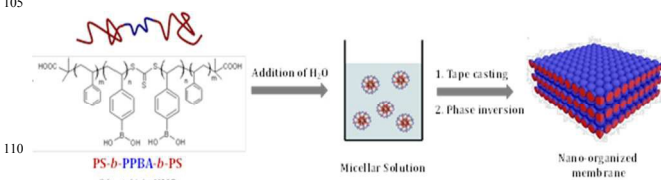
UV treatment. The self-assembled film was placed in a petri dish filled with water and replaced under a UV-lamp (OmniCure S-1000; 320-480 nm) for 90 minutes. After the irradiation time the obtained film was used with no further treatment.

Filtration test. The prepared membrane (d = 22 mm; A = 4.1 cm²) was fitted in a 10 mL filtration cell (Amicon 8010 Stirred Cell). Then the filtration cell was connected to the water reservoir and the compressed air line. The measurements were then performed at pressures between 0.1 and 4.0 bars. Permeate is collected in a beaker that is placed on an electric balance connected to a computer. The SartoConnect software would record the mass of the collected permeate at regular time intervals (10-30 seconds). All filtration experiments were performed at room temperature with dust free ultrapure water (filtered through a 400 micron filter).

Characterization. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4500 instrument capable of operating at a spatial resolution of 1.5 nm at 15 kV energy. Molecular weight of polymers were characterized by size-exclusion chromatography (SEC) (Wyatt) equipped with multiangle light scattering and differential refractive index detectors using THF as eluent. Micelle sizes were analyzed by photon cross correlation spectroscopy (PCCS) (Nanophox, Sympatec). 1H NMR spectra were recorded in either CDCl₃ or DMSO-*d*₆ using a Bruker 300 MHz spectrometer.

Results and Discussions

In our previous work [27] we have demonstrated that micellar solutions of triblock copolymer chains could be used to prepare nanostructured films/ membranes where the gaps between the closely packed micelles are the pores of the membranes.



Scheme 2. Molecular structure of the triblock copolymer, their resulting micelles and assembled nanostructure.

Here we have used RAFT polymerization to prepare triblock copolymer of polystyrene and poly(4-vinylphenyl boronic acid) with dispersity as low as 1.12 (see experimental section). After purification and drying, a 20 wt. % solution of the copolymer in

N-methyl-2-pyrrolidone (NMP) is mixed with 1 volume of water (1.0 mL copolymer Sol.: 1.0 mL H₂O) resulting in the formation of micelles in solution (Scheme 2). DLS measurements performed over the course of 20 days show stable micelles with an average hydrodynamic diameter of 125 nm.

To be able to prepare self-standing porous films from micelles, it is crucial to introduce links between the micelles. This can be achieved by appropriate functionalization of the hydrophilic block of the triblock copolymer. Here the boronic acid groups were chosen to play the role of linker via supramolecular chemistry. Since these interactions are pH-dependent, the micelle associations were studied at different pH values. Micellar solutions were prepared by addition of water at different pH (4.0, 7.0 and 12.0) to the polymer solution in NMP. Then thin films of each sample was prepared on a silicon wafer and analyzed by SEM. The SEM images suggest that despite the pH change the micelle diameter stays constant (30-50 nm) (Fig. 1). The samples prepared at pH 4.0 and 7.0 show a network of micelles (aggregates) and macro-voids. These voids are observed only when the solvents are removed entirely. The solvent removal creates mechanical stress caused by the drying of the film which contains the boronic acid groups below the pK_a (8.9) (Fig. 1a-b) [28]. At pH 12 the boronate form is predominant and gives good cohesion to the particles due to the presence of an extra OH for the hydrogen bonding. Figure 1c-d shows a smoother surface and fewer macro-voids (denser film). We believe that this change at pH 12 is due to the chemical interactions between the boronic acid groups on the surface of the micelles.

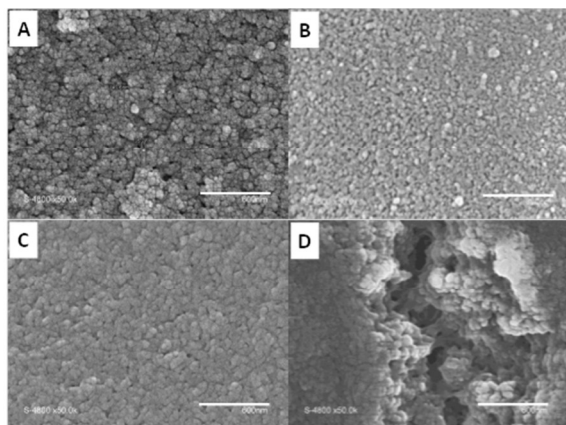


Figure 1. SEM images of BC micelle assemblies into films. Top surface of the films at (a) pH= 4 (b) pH= 7 (c) pH= 12 (d) Cross-section at pH= 12 (scale bar = 600 nm).

To prepare nanostructured porous films, a micellar solution of the triblock copolymer is cast on the surface of nonwoven polyester tissue (Fig. 2a) using a 250 μm casting knife. Then the porous film was dried in a controlled humidity environment (70% humidity). High relative humidity ensures a minimum hydration state of the film and prevents formation of macro-voids. During the drying step the micellar solution deposited on the polyester support gets concentrated (evaporation of the solvent). After 24h the film is immersed in a water coagulation bath. This step fixes/freezes the nanostructure of the porous network. Water is a bad solvent for the micelle core (PS block) and the remaining NMP (good solvent for both blocks and miscible with water) is washed out. Films prepared using this method was not good

enough for filtration test because the micellar solution has penetrated in the nonwoven support (observed by SEM). To solve this problem the nonwoven support was filled with chloroform prior to casting the polymer solution. This treatment made the support much less permeable to water and to the micelles solution thanks to the water and chloroform immiscibility. Figure 2b-c shows the top and the bottom surface of the resulting film respectively. As seen in the image (Figure 2b), the top surface is completely covered with micelles whereas the bottom surface shows macro-voids. The fractures/cracks seen on the surface of the film are due to drying during the SEM sample preparation.

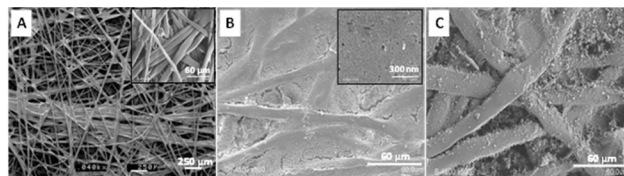


Figure 2. SEM images of (a) polyester support (b) porous film top surface supported on the nonwoven polyester tissue (c) porous film bottom surface.

The resulting porous film was then mounted in a filtration cell and conditioned at 0.1 bar for 1h prior to filtration experiments. The conditioned film was then used to filter pure water at pH 7.0 increasing the pressure gradually from 0.1 to 1.0 bar. Figure 3 shows the evolutions of flux and permeability with pressure. The permeability was found to be nearly stable up to 0.6 bar. Below 0.6bar, the flux increases slowly with increasing pressure as expected. As pressure increases above 0.6 bar, the flux increases very fast and reaches very high value ($\sim 5000 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ at 1.0 bar). This drastic change may be explained by one or a combination of the following phenomena: (1) increase in the number of pores (2) decrease of the film thickness (3) damages to the film structure (fractures). (4) increase in the pore size (5) decrease in pore tortuosity

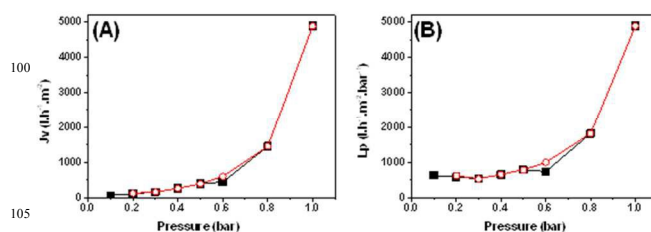


Figure 3. (a) Water flux (J_v) at pH 7 and (b) the corresponding permeability with increasing (closed black squares) and decreasing (closed red circles) pressure.

Hypotheses (1) and (2) can be rejected because the number of pores is fixed and such a significant flux increase (10 fold) would require a decrease of the film thickness to one tenth of its initial dimension (1.1 μm) according to the Hagen-Poiseuille equation (Equation S1). This would result in film dissociation. The possibility of the film being torn at high pressure (hypothesis 3) can also be ruled out because successive filtration cycles (pressurization- depressurization) are almost identical (Fig. 3). The reason for this increase in the flux is thus possibly caused by a reversible morphology change leading to a decrease in the pore tortuosity since the building blocks of the nano-structured film (micelles) are dynamically linked (Fig. 4d). Increasing the water pressure may trigger the formation of preferential water channels

within the film due to the pressure-reversible reorganization of the micelles (e.g. from compact to cubic ordering). A nonlinear fit with function x^4 gave a correlation coefficient of 0.98232 which, in agreement with the Hagen-Poiseuille equation (Eq. S1), suggests that the main contribution to the flux increase is due to the change in the pore diameter (Fig. S6). Such a porous film would exhibit 2 different pore sizes based on the operating pressure.

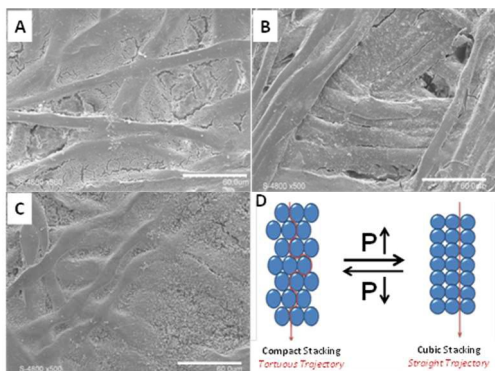


Figure 4. SEM images of porous film top surface (a) before filtration (b) after filtration of pH=7 water (c) after filtration of pH=12 water (d) schematic depiction of packing at high and low pressures. (scale bar = 60 μm)

The SEM studies of the film surface before (Fig. 4a) and after (Fig. 4b) filtration at pH 7 reveal no noticeable change in the morphology and packing of the micelles. This proves that the film is sufficiently mechanically resistant. The micelles were not removed from the polyester fibers even under the highest tested water pressures.

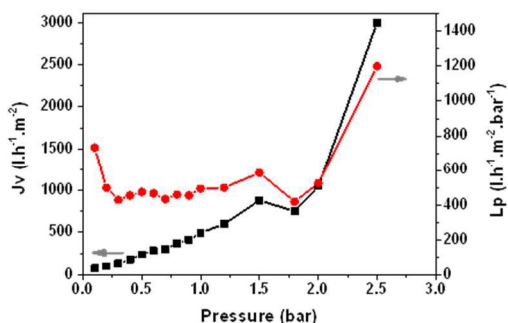


Figure 5. Water flux (J_v) at pH 12 (closed black squares) and the corresponding permeability (closed red circles) as a function of pressure.

Filtration of water at pH 12 using the same film resulted in lower flux and permeability even though a similar general behavior (relatively stable values or slow increase up to 1.8 bars followed by a sharp increase at higher pressure) was observed. As Figure 5 shows the domain of stable permeability has been extended to 1.8 bar (the stable domain at pH 7 was 0.1-0.6 bar). As a result flux and permeability could be recorded up to a higher pressure (2.5 bar). The first data point on the permeability curve (Figure 5 closed red circles) is slightly elevated compared to the data point at 0.2 bar. This might be explained by the time required for the boronate interaction to establish at pH 12 and lead to the formation of the porous film. Indeed, certain amount of water at pH 12 would need to pass through the film to complete the inter micellar interaction change among the boronic acid groups across

the film thickness.

SEM images of the film before and after the filtration of water at pH 12 is shown in Figure 4a and c respectively. Better inter micellar cohesion is observed after filtration of pH 12 water than after filtration of pH 7 water or the starting film. One can also note that in this case, the drying process does not generate cracks in the film (unlike the membrane used at pH 7- see Figure 4b). This result agrees with the preliminary observations that micelle deposits on silicon wafer show a more compact assembly at pH12 than at pH 4 or 7 (Fig. 1a-d).

To investigate the effect of UV irradiation on the cohesion of the micelles organization in the self-assembled porous film, the initial film (before filtration) was irradiated with UV for 1h30 in water before being mounted in the filtration cell. Permeability tests were then conducted at both pH 7 and 12 under the conditions described previously.

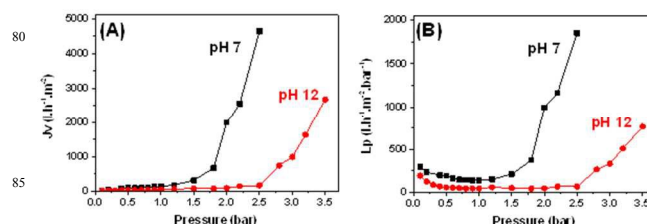


Figure 6. Filtration after UV-irradiation, (a) water flux (J_v) at pH 7 (closed black squares) and at pH 12 (closed red circles) (b) corresponding permeability at pH 7 (closed black squares) and at pH 12 (closed red circles) as a function of pressure after UV treatment.

As shown in Figure 6 at both pH values, the flux stability zone has been extended considerably compared to non-irradiated films. The UV treated film at pH 7 has now a stable flux up to 1.5 bar while the same film before the UV irradiation had only a stable flux up to 0.6 bar. The same trend is observed at pH 12 where the flux is stable up to 2.5 bar compared to 1.8 bar for non-treated film. This larger range of pressure for which both the flux and the permeability are stable suggest that the UV treatment induced a more efficient linkage between the building blocks (micelles) of the porous film, leading to an increased overall stability of the film. This increased cohesion was visually observed by SEM analysis as shown in Figure 7. The top surface of the UV treated film after filtration of pH 7 water (Fig. 7a-c) shows a smoother coverage of the polyester support compared to that of the untreated film under the same condition (after filtration of pH 7 water) (Fig. 4b).

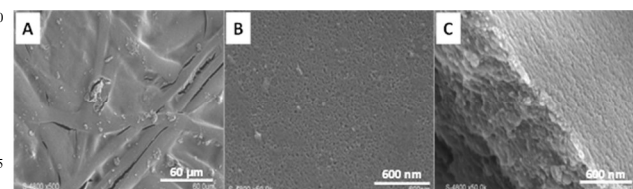


Figure 7. SEM images of UV treated film (a) top surface (b) top surface at higher resolution (c) cross-section after filtration of pH 7 water.

Conclusion

ABA triblock copolymer consisting of polystyrene and poly(4-vinylphenyl boronic acid) (PS-PPBA-PS) was prepared using

RAFT polymerisation. This well-defined triblock copolymer was then self-assembled into micelles with PPBA coronas and PS cores, and the effect of pH on their formation was investigated. A nanostructured porous film was then made by self-assembly of the micelles prepared at pH 7 on a polyester nonwoven support. The permeability of the film was studied at two pH values (7 and 12). The stability domain of the film depends considerably on the pH of the water filtered through the film. At pH 7 the stability limit is 0.6 bar while at pH 12 this limit increased to 1.8 bar. This change is likely due to stronger supramolecular interactions among the boronic acid groups present on the surface of the micelles at higher pH. Above this pressure threshold (0.6 bar for pH 7 and 1.8 bar for pH12) a considerable increase in the permeability of the porous film (> 100 fold increase) was observed. This increase was not caused by fracture of the film since successive pressurization-depressurization cycles resulted in almost identical flux values. We thus suggest that the observed behavior is caused by a reversible morphological change within the film network provoking a strong decrease in the tortuosity (the non-linear nature of the trajectories of fluid through the porous medium) of the porous network. UV treatment was also performed in order to strengthen the inter-micelle interactions via thiol exchange between the trithiocarbonate moieties present on the corona of the micelles. Stronger link between micelles would indeed enable the film to retain relatively low permeability at higher pressures. However, the micelle rearrangement could not be observed directly using SEM because the micelles return to their original state upon release of the pressure. This morphology change may be explained by the reduction of tortuosity. Based on this hypothesis, the permeating fluid causes reorganization within the porous film from compact stacking to cubic stacking at elevated pressures. Finally the effect of stability and density of the film was increased by a simple UV irradiation.

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Notes and references

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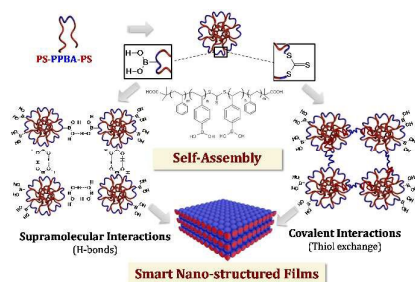
† Electronic Supplementary Information (ESI) available: Full copolymer characterization by ¹H NMR, DOSY NMR, GPC, Hagen-Poiseuille equation and water flux data of the porous copolymer films. See DOI: 10.1039/b000000x/

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Stimuli Responsive Nanostructured Porous Network from Triblock Copolymer Self-assemblies

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30-word TOC Graphic Summary:

Well controlled ABA triblock copolymer with pendent boronic acid groups is prepared using RAFT chemistry. The resulting flower like micelles in mixture of H₂O/NMP forms stimuli responsive porous network.