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Synthesis of Highly Porous Poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) Asymmetric Membranes

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For the first time, self-assembly and non-solvent induced phase separation was applied to polysulfone-based linear block copolymers, reaching mechanical stability much higher than other block copolymers membranes used in this method, which were mainly based on polystyrene blocks. Poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) (PtBA_{30k}-*b*-PSU_{14k}-*b*-PtBA_{30k}) with a low polydispersity of 1.4 was synthesized by combining step-growth condensation and RAFT polymerization. Various advanced electron microscopies revealed that PtBA_{30k}-*b*-PSU_{14k}-*b*-PtBA_{30k} assembles into worm-like cylindrical micelles in DMAc and adopts a “flower-like” arrangement with the PSU central block forming the shell. Computational modeling described the mechanism of micelle formation and morphological transition. Asymmetric nanostructured membranes were obtained with a highly porous interconnected skin layer and a sublayer with finger-like macrovoids. Ultrafiltration tests confirmed a water permeance of 555 L m⁻² h⁻¹ bar⁻¹ with molecular weight cut-off of 28 kg/mol. PtBA segments on the membrane surface were then hydrolyzed and complexed with metals, leading to cross-linking and enhancement of antibacterial capability.

Introduction

The fabrication of highly ordered, asymmetric isoporous membranes based on block copolymers using self-assembly combined with conventional non-solvent induced phase separation was first reported by Peinemann et al.¹ Although there is a wide body of literature on block copolymer films and membranes,^{2–5} given that no additional annealing or etching step is needed with the new proposed method, this was a great step towards large-scale manufacture. The mechanism could only be understood later, after recognizing the role of supramolecular micelle assemblies in the formation of the nanoporous membranes.^{6–11} The potential of these flexible membranes has been demonstrated by several studies mainly based on poly(styrene)-*b*-poly(4-vinyl pyridine) copolymers (PS-*b*-P4VP) with practical applications varying from catalysis,¹² antibacterial filtration,¹³ to selective separation¹⁴ and controlled release¹⁵ of proteins.

This method, now referred as “self-assembly and non-solvent induced phase separation” (SNIPS),¹⁶ is simple, reproducible and compatible with existing technical machines. Recently, the SNIPS strategy has been expanded to other diblock or triblock copolymers beyond PS-*b*-P4VP.^{17–21} However all copolymers

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used in SNIPS so far have polystyrene as the main component. Polystyrene is easy to copolymerize by different methods and in combination with hydrophilic blocks is known to self-assemble in different solvents and in the bulk.²² A common disadvantage of polystyrene-based membranes is their lower mechanical stability, when compared to homopolymers like polysulfone and polyvinylidene fluoride, traditionally used in membrane manufacture. Moreover, the low glass transition temperature (T_g) of polystyrene (100 °C) limits the thermal stability of such membranes. To overcome these drawbacks, a few tailor-made block copolymers have been proposed in an attempt to improve stability. One approach is the substitution of polystyrene with poly(*tert*-butyl styrene) (PtBS) and poly(4-trimethylsilyl styrene) (PTMSS) that have higher T_g to improve the thermal and chemical stability.¹⁸ Another example is the incorporation of rubbery polyisoprene (PI) block into hydrophobic domain to toughen the PI-*b*-PS-*b*-P4VP triblock terpolymer membrane.¹⁹ However polystyrene or derivatives in both cases remains the major monomer and improvements are only incremental.

Here we report novel nanostructured membranes *via* SNIPS, made from polysulfone-based triblock copolymer, poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) (PtBA-*b*-PSU-*b*-PtBA) for the first time. Polysulfone (PSU) is one of the most widely used polymer families for membrane fabrication, featuring good pore forming property, high resistance in extreme pH conditions and chlorinated disinfectants, and excellent mechanical strength and thermal stability with a T_g of 190 °C.²³ The incorporation of PSU within the block copolymer membranes will open the door to more demanding applications due to their increased robustness. Nevertheless, the difficulty lies in the fact that polysulfone can be synthesized only by step-growth polycondensation, rendering broad molecular weight distribution.²⁴ Even worse is that block copolymers are normally unachievable using this technique. In order to obtain polysulfone-based triblock copolymer with reasonable polydispersity required for ordered micro-phase separation, we combined the condensation and reversible addition fragmentation chain transfer²⁵ (RAFT) polymerization. To the best of our knowledge, this is the first SNIPS contribution using copolymers containing blocks of high-performance engineering resin such as polysulfone for membranes. Therefore, we believe this synthetic methodology will expand the material arsenal for SNIPS membranes with improved performance and enriched functions.

Results and discussion

Synthesis of PtBA-PSU-PtBA Triblock Copolymer

Scheme 1 depicts the reaction procedure aiming at poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) (PtBA-PSU-PtBA) triblock copolymer. The difficulty in synthesizing well-defined block copolymers comprising of step-growth condensation and vinyl polyaddition segments arises from the distinct nature of the respective polymerization mechanisms. This difference can be bridged by mechanistic transformation

Scheme 1. Synthesis route of Poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) (PtBA-PSU-PtBA).

techniques,^{26, 27} in which a polymer chain synthesized by a certain mechanism is functionalized for the initiation of consecutive polymerization through another mechanism. In the present work, a hydroxyl-terminated telechelic polysulfone was prepared by polycondensation of bis(4-chlorophenyl) sulfone with an excess of diol monomer, bisphenol-A, according to the literature.²⁴ The hydroxyl chain-end functionality may be facilely transformed to the initiating site for chain-growth polymer on the polysulfone backbone, which serves as the central block of the triblock copolymers. For the subsequent chain extension step, reversible-deactivation radical polymerization (RDRP) is commonly used to afford complex macromolecular architectures with a well-controlled manner. For example, after the hydroxyl group was converted to an atom transfer radical polymerization (ATRP) alkyl halide initiator, *n*-butyl acrylate,^{28, 29} styrene,²⁸ poly(ethylene glycol) methyl ether methacrylate (PEGMA),³⁰ 3-O-methacryloyl-1,2:5,6-di-O-isopropylidene- α -D-glucopyranose (MALpG),³⁰ 2,3,4,5,6-pentafluorostyrene,^{31, 32} methyl methacrylate,³² and the ionic liquid monomer, 1-(4-vinylbenzyl)-3-butylimidazolium bis(trifluoromethylsulfonate) imide (VBBI⁺Tf₂N⁻)³² were successfully polymerized from the polysulfone macroinitiators to generate the outer blocks. Yet another important RDRP technique, RAFT polymerization has not been fully exploited to prepare polysulfone-based triblock copolymers. Only Yi et al.³³ reported the synthesis of PPEGMA-*b*-polyethersulfone (PES)-*b*-PPEGMA with the PES macro-CTA formed by an esterification of the hydroxyl end group with a carboxyl-functional trithiocarbonate RAFT agent. In this study, we applied this RAFT methodology to obtain PtBA-PSU-PtBA triblock copolymer, which has not been reported in the literature so far.

As shown in Scheme 1, the α , ω -dihydroxyl-terminated polysulfone from condensation, was reacted with a carboxylic acid-terminated RAFT agent, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid using N,N' -dicyclohexylcarbodiimide (DCC) as a coupling reagent and 4-(dimethylamino)pyridine (DMAP) as a catalyst to obtain the trithiocarbonate RAFT chain transfer agent-capped polymer, CTA-PSU-CTA as an esterification product.³⁴ ^1H NMR spectra are given in Figure 1 for HO-PSU-OH, CTA-PSU-CTA and PtBA-PSU-PtBA. The chemical shifts at $\delta = 6.74$ -7.85 ppm (Figure 1a) are assigned to the aromatic protons of the PSU backbone, among which two small doublets centered at 6.75 and 7.09 ppm belong to the protons located at ortho and meta position to $-\text{OH}$ in the terminal phenyl rings, respectively. The peak at 1.74 ppm is attributed to aliphatic protons of the isopropylidene. After esterification with RAFT agent, the complete end group functionalization can be confirmed by the emergence of new protons corresponding to the CTA groups,³⁵ as indicated by the CTA-PSU-CTA NMR spectrum in Figure 1b. The subsequent RAFT polymerization towards triblock copolymer PtBA-PSU-PtBA was carried out with [AIBN]: [CTA-PSU-CTA]: [tBA] = 1: 3: 1800 in DMAc at 80 °C for 24 hrs. Figure 1 confirms the successful polymerization by a peak corresponding to methylidyne protons ($-\text{CH}_2-\text{CH}(\text{CO}_2)-$) on the PtBA main polymer chain at $\delta = 2.15$ ppm, and broad peaks from 0.9 to 1.67 ppm corresponding to the methylene ($-\text{CH}_2-\text{CH}(\text{CO}_2)-$) and *tert*-butyl protons ($-\text{CO}_2\text{C}(\text{CH}_3)_3$). ^{13}C NMR spectra and assignment can be found in Figure S1 (supporting information). Furthermore, the presence of PtBA block is confirmed by the strong peak for ester C=O stretch at 1723 cm^{-1} in the FTIR spectrum (Figure 2), increased peak intensity for

Figure 1. ^1H NMR spectra for HO-PSU-OH, CTA-PSU-CTA, PtBA-PSU-PtBA recorded in CDCl_3 .

alkyl C-H stretch on the PtBA main chain in the region 2800-

Figure 2. FTIR spectra for (a) HO-PSU-OH and (b) PtBA-PSU-PtBA.

3150 cm^{-1} and C-H bending of $\text{C}(\text{CH}_3)_3$ at 1367 cm^{-1} .^{36, 37} Absorption bands related to the PSU macro-CTA are also visible in the spectrum of triblock copolymer, e.g. 1294 , 1150 and 1080 cm^{-1} for $-\text{S}(\text{O}_2)-$, and 1584 and 1488 cm^{-1} for aromatic C-C stretch.^{38, 39}

The GPC curves for polysulfone homopolymer and PtBA-PSU-PtBA triblock copolymers are shown in Figure 3. The peak after RAFT copolymerization has a clean shift to shorter retention time than the homopolymer, indicating higher molecular weight. The GPC curve for PtBA-PSU-PtBA is monomodal without any apparent shoulder, which suggests that the CTA moiety was coupled onto the polysulfone chain ends with high

Figure 3: GPC curves with refractive index detector (RI) and the corresponding parameters for HO-PSU-OH and PtBA-PSU-PtBA. $^a M_{n,\text{NMR}}$ for HO-PSU-OH was calculated from the integral of ^1H NMR peak for ortho hydrogen on terminal phenol ($\delta=6.75\text{ ppm}$); $^b M_{n,\text{NMR}}$ for PtBA-PSU-PtBA was determined by taking into consideration the $M_{n,\text{NMR}}$ for HO-PSU-OH and f_{PtBA} , calculated from the integral of ^1H NMR peak for $-\text{CHCH}_2-$ on PtBA backbone ($\delta=2.15\text{ ppm}$).

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yield and was later the functionality used for RAFT polymerization. Notably, the molecular weight distribution of triblock copolymer is narrower than the PSU obtained from polycondensation, as the polydispersity decreases from 2.1 to 1.4, due to the incorporation of well-defined PtBA side blocks. This phenomenon has been observed for ATRP as well.²⁸ The number-average molecular weight of polysulfone determined by NMR is 14.4 kg mol^{-1} , lower than the commercial Udel polysulfone ($\sim 30 \text{ kg mol}^{-1}$) that is commonly used for membrane fabrication, because the degree of polymerization is limited by the difference in stoichiometry between monomers according to the Carothers equation.⁴⁰ This value agrees with the M_n measured by GPC using 99 kg mol^{-1} polystyrene standard. A comparison between the integral of protons on PtBA backbone in NMR and that of PSU protons gives the weight fraction of PtBA segment (f_{PtBA}), which is 80 %. Based on that, the molar mass of PtBA was calculated as 58 kg mol^{-1} , and the total molar mass of PtBA-PSU-PtBA as 74.8 kg mol^{-1} , higher than M_n determined by GPC (Figure 3) which implies hydrodynamic size cannot reflect the true molar mass of copolymer.

Figure 4. TGA curves for HO-PSU-OH, CTA-PSU-CTA and PtBA-PSU-PtBA under N_2 .

The thermal properties of the polymers were evaluated by measuring their thermal decomposition and glass transition temperature. Figure 4 shows the TGA curves of the polysulfone precursor, end-group functionalized macro-CTA and PtBA-PSU-PtBA triblock copolymer. PSU homopolymer exhibits a sharp weight loss starting from 450°C which demonstrates its high thermal stability. After end-group functionalization, the CTA-PSU-CTA has a small weight loss from 200 to 330°C corresponding to the thermal homolysis of C-S bonds in the anchored RAFT agent.⁴¹ A multi-stage weight loss profile can be observed from PtBA-PSU-PtBA thermogram, consistent with the experimental data reported by literature.^{42, 43} It begins with the initial elimination of *tert*-butyl group at 220°C , which releases isobutylene. The produced carboxylic acid groups on the backbone dehydrate to give six-member cyclic anhydride structure and water. When heated up to 250°C ,

the degradation of the side group or PtBA backbone leads to a gradual weight loss, followed by the decomposition of PSU mid-block. Estimated from the TGA curve of HO-PSU-OH and PtBA-PSU-PtBA, the weight loss caused by PtBA block is around 80 wt%, correlated well with the weight fraction obtained from ^1H NMR. The glass transition temperature of HO-PSU-OH is determined by differential scanning calorimetry (DSC) to be approximately 167°C . PtBA-PSU-PtBA displays only one transition at about 46°C which belongs to PtBA. There is no detectable T_g originating from PSU block probably due to its low fraction in the triblock copolymer. The DSC curves are shown in Figure S2, supporting information.

Formation of Nanostructured Membranes via SNIPS

We used the synthesized PtBA-PSU-PtBA triblock polymer to fabricate asymmetric membranes *via* the SNIPS technique.¹⁶ Our previous studies have demonstrated that in this process the block copolymer micellization and the micelle supramolecular assembly in solution play a decisive role for the pore formation in the upper layer of the membrane. The morphology starts to be induced even before immersion in water. Different than in other explored cases, instead of AB diblock copolymers,^{1, 7, 9-11} the present work uses an amphiphilic BAB triblock copolymer in a selective organic solvent, whose middle block (A) is solvophilic, while the two outer blocks (B) are relatively solvophobic.

Table 1. Values of Hansen solubility parameter for polymer segments and solvents

	$\delta^a [\text{MPa}]^{1/2}$				$\chi_{\text{polymer-solvent}}$
	δ_D	δ_P	δ_H	δ_T	
PtBA	16.0	2.3	3.1	16.4	1.35
PSU	16.6	6.0	6.6	18.8	0.49
DMAc	16.8	11.5	9.4	22.4	--
H_2O	15.5	16.0	42.3	47.8	--

^a δ of PtBA is calculated by HSPiP software 4th Edition, others are cited from reference 44, $\delta_T = (\delta_D^2 + \delta_H^2 + \delta_P^2)^{1/2}$

BAB copolymer micellization with flower-like organization. 20 wt% of the synthesized $\text{PtBA}_{30\text{k}}\text{-PSU}_{14\text{k}}\text{-PtBA}_{30\text{k}}$ was dissolved in N,N-dimethylacetamide (DMAc). The Flory-Huggins interaction parameters (χ) can be estimated, by using Hansen solubility parameters (δ).⁴⁴ Table 1 shows the different contributions to δ (i.e., dispersion force (δ_D), polarity (δ_P), and hydrogen bonding (δ_H)), and the computed interaction parameter $\chi_{\text{polymer-solvent}}$ between each polymer segment and solvent pairs in the casting solution. From Table 1, it is evident that DMAc is a selective solvent for the polysulfone block, whereas the interaction with the poly(*tert*-butyl acrylate) is poorer. To avoid the less favorable PtBA contact with DMAc, the block copolymers are expected to assemble into a "flower-like" morphology, as depicted in Figure 5a. The middle PSU blocks form loops, which constitute the corona and the PtBA blocks segregate into the micelle core. The self-assembly of other BAB copolymers has been investigated before⁴⁵⁻⁴⁷ and the existence of flower-like micelles have been demonstrated.^{48, 49}

Figure 5. (a) Schematic illustration of flower-like micelles formed by BAB triblock copolymer: red represents the two end PtBA blocks, while blue denotes the middle PSU block; (b) Cryo field emission scanning electron microscopy (cryo-FESEM) image for worm-like cylindrical micelles in solution (20 wt% PtBA-PSU-PtBA in DMAc) with a diameter of about 30 nm; (c) DPD simulation of the effect of the BAB copolymer concentration and size of block A over the morphology of the assembled micelles. The blue contours correspond to block A, whereas the red particles represent block B. The solvent representation as particles was removed to facilitate the visualization.

The free energy G of this type of corona-core structures can be expressed Equation 1,

$$G = G_{\text{corona}} + G_{\text{core}} + G_{\text{interface}} \quad (1)$$

where the G_{corona} and G_{core} account mainly for the stretching of block segments from their unperturbed condition to the conformation they assume in the corona and core; $G_{\text{interface}}$ is related to the formation of the PtBA-PSU and PSU-solvent interfaces. The interfacial free energy typically depends on the total interfacial areas ($A_{\text{interface}}$) and the interfacial tensions (γ) as Equation 2.

$$G_{\text{interface}} = \gamma A_{\text{interface}} \quad (2)$$

During the formation of flower-like micelles the reduction of the total interfacial free energy competes with the entropic penalty caused by looping middle block. To alleviate the entropy loss, some of the B blocks might dangle in solution, or associate into neighboring micelles to form a branched structure bridged by polymer chains of well-solvated block.^{45, 50, 51}

Worm-like cylindrical micelle formation. Cryo-electron microscopy (cryo-EM) is a powerful tool to directly reveal the morphology of block copolymer micelles in solution.⁶ Figure 5b shows the cryo field emission scanning electron microscopy (Cryo-FESEM) image of a fractured droplet of a 20 wt% PtBA-PSU-PtBA casting solution in DMAc. This image shows that triblock copolymers assemble into worm-like cylindrical micelles with a diameter of around 30 nm, distributed in a random network. Some interconnected or fused strings suggest the coexistence of branched structures besides the isolated micelles.

Spherical geometry has been reported for flower-like micelles of BAB triblock copolymers.^{48, 49} We believe the formation of cylindrical morphologies in this work is a consequence of the increase of the micelle size, reflected in the aggregation number (N_{agg}) and micelle core size (R_{core}). The growth of micelles is energetically favorable because it decreases the total interfacial area ($A_{\text{interface}}$), minimizing the free energy contribution $G_{\text{interface}}$. However, as the size of the micelles increases the stretching of the core-forming blocks imposes an entropic penalty over the free energy G_{core} . As N_{agg} grows, the assembly of the copolymer chains into spherical micelles requires a high degree of stretching of the PtBA core-forming blocks. Thus, non-spherical micelles are preferred in order to reduce the deformation energy needed (G_{core}) to confine them into the core.

Competing entropic (affected by the composition of the triblock copolymer and polymer concentration) and enthalpic (affected by the polymer-solvent interactions) contributions determines the total free energy G .²² In particular, for the casting solutions used to prepare the membranes, we found that the balance of these effects on G stabilizes the assemblies shapes illustrated in Figure 5. The shape of amphiphiles assemblies in solution is usually correlated to the packing parameter, p ,

$$p = v / (a_0 l_c) \quad (3)$$

where v and l_c is the chain volume and length of core block, respectively, and a_0 is the optimum surface area of corona block at the interface. Spherical micelles are formed when $p \leq 1/3$. When p increases to about 0.5, rods or cylinders are preferred. At higher p (0.5~1), they evolve to interconnected networks.⁵² In order to better rationalize the formation of cylindrical assemblies we model the self-assembly of a triblock copolymer BAB in a selective solvent favorable for A, as illustrated in Figure 5c. To construct the computational model we use the dissipative particle dynamics (DPD) method. We refer the reader to the Supporting Information for a detailed description of the DPD computational model.

The polymer concentration in the casting solution strongly influences the morphology. In general, an increase of

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copolymer concentration leads to micelle growth with a corresponding increase in N_{agg} and R_{corona} .⁵³ A further increase of concentration might induce a morphological transition to non-spherical micelles. Our computational model captures this concentration effect in the simulations. Figure 5c shows the morphological transition of assemblies from spherical to an interconnected network as the polymer concentration increases, simulated by DPD. In addition to the overall polymer concentration, the block lengths of PtBA-PSU-PtBA affect the assembly morphology.²² In our systems we have micelles with a relatively small corona, due to the low fraction of PSU in the block copolymer. This facilitates the fusion of spherical micelles into a network with elongated cores at large copolymer concentrations. In contrast, when the length of the middle block is larger, thicker coronas are formed and the fusion of micelle cores becomes entropically less favorable. We demonstrate this effect by modeling the morphological transitions of a copolymer $B_{20k}A_{21k}B_{20k}$, which has the same total molecular weight as the copolymer experimentally used in this study ($B_{30k}A_{14k}B_{30k}$), but has a larger fraction of A. Figure 5c shows the formation of assemblies with larger N_{agg} in the form of a network. As the polymer concentration increases, larger A blocks favor the formation of a network constituted by a fused corona and an array of segregated cores.

Figure 6. FESEM of PtBA-PSU-PtBA membrane (a) surface and (b) cross-section; TEM of PtBA-PSU-PtBA membrane cross-section near the (c and d) top surface and (e) bottom.

Similarly to the copolymer block length, the polymer-solvent interactions can change the dimension of both core and corona domains, modifying the final morphogenesis of the assemblies.⁵⁴ Herein, DMAc prefers PSU blocks, however, because of partial solubility of PtBA homopolymer in DMAc, some degree of core swelling is expected. The core swelling facilitates the formation of elongated assemblies, which interconnect in a network. The similar phenomenon related to the solvent has been described by Quémener et al.⁵⁵ In their work, by increasing the content of toluene in the mixed

solvent with DMF, the shape of poly(styrene-co-acrylonitrile)-*b*-poly(ethylene oxide)-*b*-poly(styrene-co-acrylonitrile) flower-like micelles changed from spherical nanoparticles to a worm-like network, similar to those structures we obtained for PtBA-PSU-PtBA copolymer.

Membrane formation by immersion in water. Water is a nonsolvent for PtBA-PSU-PtBA. All solubility parameter contributions for water are far from those of rather hydrophobic PtBA and PSU blocks (Table 1). When the solution is cast as a thin film and immersed into water, a fast solvent-water exchange leads to an abrupt decrease of chain mobility fixing the polymer-polymer entanglement and kinetically trapping the morphology formed in solution. Therefore, the worm-like cylindrical morphology on the top of the solution layer is completely immobilized, giving rise to the nanostructured membrane with a highly porous surface. Field-emission scanning electron microscopy (FESEM) was employed to investigate the membrane surface and the image shown in Figure 6a confirms the correlation between the interconnected 3D porous structure of the triblock copolymer membrane and the worm-like network formed by cylindrical micelles in the bulk of the solution before immersion. DMAc is rapidly replaced by water. A network of assembled copolymer will form the membrane matrix and the pore walls. The space in between, which is depleted in copolymer, will be filled by water. Solvent-water exchange proceeds in layers far from the water-copolymer solution interface, but at a lower rate, because the water and solvent will have to be transported through the already solidified top layer. As the water content increases a macroscopic phase separation is induced. Macrophase separation follows the mechanism of spinodal decomposition and/or nucleation and growth, similar to what happens with homopolymer solutions in the formation of asymmetric membranes. The polymer-poor phase forms the pores and the polymer-rich phase forms the membrane structure fixed by gelation/solidification, when the polymer concentration in this phase is high enough. The membrane top layer is fast solidified, immediately after immersion in water, before the macrophase separation even starts. On the other hand, far from the water-solution interface, phase separation proceeds to a further extent before solidification starts, leading to larger segregated phases (incipient pores). Based on this principle, an asymmetric membrane is expected. Indeed, the FESEM image for the membrane cross-section (Figure 6b) confirms a pronounced asymmetry: a high density of small pores is seen on the top (see high magnification image in the inset) and disordered, larger pores predominate the part underneath the top layer. Moreover, long finger-like macrovoids extending to the bottom show up on the cross-section, which are not observed in PS-*b*-P4VP nanoporous membranes. They frequently appear in the commercial phase inversion membranes manufactured from homopolymers. This highly porous asymmetric structure spanning from top to bottom with the coexistence of sponge- and finger-like pores is also supported by TEM as shown in Figure 6c-e.

This membrane is promising for filtration application with pore size in the ultrafiltration (UF) range (2~50 nm) and high porosity resulting from the micelle network. Mechanical stability is also an important quality for membrane application. The typical stress-strain curves from dynamic mechanical analysis (DMA) tensile test for PSU homopolymer and PtBA-PSU-PtBA triblock copolymer membranes prepared under same conditions are plotted in Figure 7. The Young's modulus (E) and ultimate stress of PSU are higher than those of copolymer, while the maximum elongation of copolymer is larger. It shows that the presence of low T_g (46 °C) PtBA domain renders a more ductile membrane, allows the

Figure 7. Stress-strain curves for HO-PSU-OH and PtBA-PSU-PtBA membranes.

membrane to be deformed to a larger extent, whereas the stress resistance is slightly compromised compared to the PSU membrane which is more rigid. The area under the stress-strain curve of copolymer membrane, representing its toughness, defined as the maximum energy a material can absorb before rupturing, is 607 kJ m⁻³, doubles that of 306 kJ m⁻³ toughness of PSU membrane. Phillip et al.¹⁹ reported for PS-*b*-P4VP and PS-*b*-PI-*b*-P4VP maximum stress values similar to those measured in this work, but with strain values lower than 0.5 %. For OH-PSU-OH and PtBA-PSU-PtBA membranes we reached strain values up to 28 %. This leads to toughness values, which are 34 to 67-fold higher for PSU-based copolymers than for the polystyrene-based ones. Toughness values reported for another previously reported membrane based now on polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide),²¹ are two orders of magnitude lower than that of the PSU-block membrane.

Hydrolysis and Metal Complexation of Membranes

PtBA can be easily hydrolyzed into poly(acrylic acid) (PAA) by acid treatment, or by using ZnBr₂ without acid.⁵⁶ This dramatically increases the hydrophilicity of the copolymer and the prepared membranes. However since the PSU block is

relatively small, the pure hydrolysis leads then to films, which can highly swell in water, behaving like a gel and not being convenient for membrane applications. We found out that if the hydrolysis is immediately followed by complexation with transition metal ions, e.g. Cu²⁺ and Fe³⁺, stable hydrophilic porous membranes are formed with a surface morphology different than that before the modification. Figure 8d describes the procedure for modification and the possible structures of PAA-metal complexes.⁵⁷ Partial hydrolysis of *tert*-butyl ester units on the surface of membrane, by treating with concentrated hydrochloric acid (HCl) aqueous solution (37 %, w/w), leads to the formation of carboxylic acid groups, analogous to reports for other copolymers containing PtBA.⁵⁸ The hydrolysis time has been optimized to achieve sufficient surface hydrolysis without damaging the bulk membrane strength. Then the membrane was taken out of the acid bath and plunged into a solution containing 0.1 M Cu²⁺ or Fe³⁺ metal

Figure 8. (a) Photographs of PSU-PAA-Cu²⁺ (top) and PSU-PAA-Fe³⁺ (bottom) membranes in dry state and immersed in DMF (insets); (b) FTIR spectra and (c) contact angle measurement for original (i) PtBA-PSU-PtBA, (ii) PSU-PAA-Cu²⁺ and (iii) PSU-PAA-Fe³⁺ membranes; (d) Surface modification of PtBA-PSU-PtBA membrane via hydrolysis and metal complexation.

solution. The product of hydrolysis, the poly(acrylic acid) (PAA) segment, is well known as anionic polyelectrolyte capable of complexing metals.⁵⁹ Functional membranes taking advantage of this property for separation purposes have been reported. For instance, Weidman et al. hydrolyzed polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) nanostructured membranes to obtain pores with exposed PAA blocks for

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selective separation of copper over nickel ions.⁶⁰ Binding of a

Figure 9. (a) Surface and (b) cross-sectional FESEM images of PSU-PAA-Cu²⁺, and (e and f) PSU-PAA-Fe³⁺; The insets are EDS spectra recorded from the corresponding membrane surface; TEM elastic electron images of (c) PSU-PAA-Cu²⁺ and (g) PSU-PAA-Fe³⁺, and energy loss element specific image of (d) PSU-PAA-Cu²⁺ (Cu-L edge at 931 eV) and (h) PSU-PAA-Fe³⁺ (Fe-L edge at 721 eV), obtained with inelastic electron.

series of metal ions to PAA has been investigated at various degrees of dissociation, indicating also the formation of multidentate ligand complexes⁶¹, which would explain the crosslinking of membrane, as illustrated in Figure 8d. The intermolecular polymer-metal binding has been utilized to form hydrogels⁶² for dental application. Recently the complexation of thiourea- and triazole-based polymers with different metal ions has been used to induce phase inversion and fabricate high metal loading membranes with thin selective layer.^{63, 64} The complexation of metals in our case can be visualized by the strong color of the Cu(II)- (blue) and Fe(III)-complexed membranes (brown), denoted as PSU-PAA-Cu²⁺ and PSU-PAA-Fe³⁺, respectively (see Figure 8a). The insets in Figure 8a show that when immersed in DMF, a good solvent for the parent triblock copolymer, these two membranes were not

dissolved thanks to the crosslinking. They just swell and become more transparent. FTIR spectra of the metal complex membranes are shown in Figure 8b and display a broad band at 3000-3850 cm⁻¹ due to the stretching vibration of O-H groups in PAA units from the hydrolysis of PtBA. As we expected, the presence of negatively charged PAA and metal ions on the surface made the membrane more hydrophilic. The contact angle of PSU-PAA-Cu²⁺ and PSU-PAA-Fe³⁺ membrane dramatically decreased to 39.8 ° and 13.5 ° respectively from 120.9 ° of the original membrane comprising of hydrophobic PSU and PtBA before hydrolysis, as shown in Figure 8c. The weight fractions of Cu²⁺ and Fe³⁺ were found to be 1.4 % in the metal-complexed membranes by analyzing their TGA curves and assuming that the metal ions were fully converted to their oxides, when heated in air (Figure S3 in supporting information). Beside copper and iron, various transition metals were able to form complex with the PAA block in the membrane. This can be seen by the different colors of membranes exposed to different metals under the same condition (Figure S4 in supporting information).

By comparing Figures 6a to 9a and 9e it is clear that the membrane surface morphology significantly changed. The membranes after hydrolysis and complexation are smoother. The membranes prepared by complexation with Cu²⁺ have more regular pores and the pore density is higher than by complexation with Fe³⁺. We believe that during the hydrolysis, as the PtBA blocks are transformed into PAA, the cores become highly swollen. Since the PAA blocks constitute the higher fraction of the membrane, in contact with water the previous structure dominated by “flower-like micelles” tends to invert near the surface, re-arranging the surface morphology and switching the membrane hydrophilicity. If the complexation of the PAA carboxylate anions with metal ions like Cu²⁺ and Fe³⁺ is immediately promoted, a physical crosslinking takes place and the anions becomes less available to interact with water. Water uptake is then suppressed. This de-swelling effect has been reported in PAA-containing hydrogels.⁶⁵ Also, the more rigid cross-linked PAA structure becomes less expanded or swollen than in the case of the free polyelectrolyte without metal ions. Along with FESEM, the surface elemental analysis was carried out by energy-dispersive X-ray spectroscopy (EDS). The spectra strongly indicate the presence of metals at 0.94 keV for copper L α and 0.705 keV for iron L α in PSU-PAA-Cu²⁺ and PSU-PAA-Fe³⁺ membranes, respectively (insets in Figures 9a and 9e). Electron energy loss spectroscopy (EELS) and the corresponding element specific image coupled with TEM (Figures 9c-d and 9g-h) confirm the presence and homogeneous distribution of copper and iron in the membranes. The cross-sectional FESEM images (Figures 9b and 9f) show that the morphology far from the surface did not change. The same asymmetric macroporous structure can be seen. In a control experiment, when we transferred the hydrolyzed membrane from the acid bath to a pure water bath directly, without metal ion, the membrane immediately became a transparent film and too soft to handle because of the quick deprotonation and water swelling. Figure 9e suggests that the porosity of PSU-PAA-Fe³⁺

seems to be lower than that of copper-complexed membranes. The surface of the PSU-PAA-Fe³⁺ membrane is however more hydrophilic, indicated by lower contact angle. This difference can be explained by the stronger complexation ability of Fe³⁺⁶⁵, which acts as a stronger driving force to expose the PAA segments from the micelle core to the surface in contact to water. Furthermore Fe³⁺ has higher valence than Cu²⁺ and smaller ionic radius⁶⁶ and this also helps its diffusion into membrane to complex and promote the crosslink.

Table 2. Summary of membrane ultrafiltration performance

Membrane	MFP size (nm)	PWP (L m ⁻² h ⁻¹ bar ⁻¹) ^b	MWCO _{PEG} (kg mol ⁻¹) ^c
PtBA-PSU-PtBA	30.4 ± 1.4	555 ± 176	28
PSU-PAA-Cu ²⁺	-- ^a	653 ± 191	60
PSU-PAA-Fe ³⁺	-- ^a	131 ± 6	8

^a Too brittle to measure mean flow pore (MFP) size in the dry state; ^b pure water permeance; ^c molecular weight cut-off (MWCO) for 90 % PEG rejection (Figure S5).

Ultrafiltration Performance and Anti-bacterial Activity of Membranes

The results of ultrafiltration experiment for the original PtBA-PSU-PtBA membrane and two cross-linked membranes containing copper (II) and iron (III) respectively were summarized in Table 2. The pure water permeance (PWP) of PtBA-PSU-PtBA membrane is 555 L m⁻² h⁻¹ bar⁻¹. Its molecular weight cut-off (MWCO) determined by poly(ethylene glycol) (PEG) filtration test is 28 kg mol⁻¹. This means that the smallest PEG that the membrane can effectively reject has a hydrodynamic diameter of 8 nm, calculated using an empirical equation as reported by Lentsch et al.⁶⁷ Considering the MWCO, its water permeance is much higher than common UF membranes. For instance, Zhou et al. reported 30 and 10 L m⁻² h⁻¹ bar⁻¹ for polysulfone and regenerated cellulose membranes (MWCO 30 kg mol⁻¹) respectively, purchased from Hydration Technology Innovations (HTI), LLC (Albany, OR);⁶⁸ Kanagaraj reported 52 to 94 L m⁻² h⁻¹ bar⁻¹ for polyvinylpyrrolidone-blended polyetherimide membrane (MWCO 45 kg mol⁻¹).⁶⁹ The high water flux can be attributed to the porous structure with an exceptionally high porosity. When measuring the pore size on the membrane selective layer by capillary flow porometry we obtained values of 30.4 ± 1.4 nm (mean flow pore or MFP size) with a narrow distribution as shown in Figure S6. This value is obviously larger than the PEG hydrodynamic diameter corresponding to its MWCO. The reason is the presumption of capillary flow porometry measurement that all surface pores are separated close to the perfect cylindrical pores fails when applied to the PtBA-PSU-PtBA membrane containing a highly interconnected porous morphology on the top selective layer. The analysis of the high magnification FESEM image reveals that the membrane has a wide range of pore size from sub-10 nm to above 50 nm in the 3D interconnected porous structure.

The smallest pores inside the porous network are responsible for the retention of low molecular weight PEG. Although small solutes can go through the surface pores larger than their hydrodynamic size, they are trapped by the underneath "spider web". The PSU-PAA-Cu²⁺ membrane exhibits a slightly higher water flux while its MWCO is the double of that of the parent membrane. The improved hydrophilicity could be a reason for this result. On the other hand, the water flux and MWCO of PSU-PAA-Fe³⁺ decreases dramatically to 131 L m⁻² h⁻¹ bar⁻¹ and 8 kg mol⁻¹ due to the lower porosity and higher cross-linking.

Figure 10 shows that the number of viable bacterial cells attached on PSU-PAA-Cu²⁺ membrane decreased by about 25.1% when compared to the ones on PtBA-PSU-PtBA membrane. This observation is in agreement with the previous works that demonstrated copper to exhibit antibacterial effects.⁷⁰⁻⁷² FESEM images reveal more bacteria attached on PtBA-PSU-PtBA membrane compared to PSU-PAA-Cu²⁺ membrane, which further verifies the antibacterial efficacy.

Figure 10. The number of viable bacterial cells attached on membrane surface and counted by flow cytometry; FESEM images of corresponding membranes after exposure to *Pseudomonas aeruginosa* PAO1 for 24 h.

The decrease in the number of viable cells on membranes chelated with copper as demonstrated by both flow cytometry and FESEM confirms that the presence of copper can inhibit the attachment of bacteria onto the membrane surface, which is one of the key initiation steps in biofouling.⁷³

Experimental

Materials

Polysulfone (average M_n ~22,000 g/mol, Aldrich) and potassium carbonate (K₂CO₃, Aldrich) was dried overnight in vacuum oven prior to use. Bis(4-chlorophenyl) sulfone (DCDPS, 98%, Aldrich) was recrystallized twice from hot toluene (DCDPS: Toluene = 1:1.1) prior to use. Bisphenol-A (BPA, 99%,

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Aldrich) was recrystallized twice from hot toluene (BPA: Toluene = 1:5.3). The crystals were dried at 75 °C for 12h, cooled, well powdered and dried again for 12h at 90°C⁴⁰. *Tert*-butyl acrylate (tBA, > 99%, Alfa Aesar) was extracted three times with 5% NaOH and six times with water. The organic layer was dried over NaSO₄, filtrated and then distilled under reduced pressure (60 °C/60 mmHg). 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich) was recrystallized twice from hot methanol. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (97%, Aldrich), 4-(dimethylamino)pyridine (DMAP, ≥ 99%, Fluka), N,N'-dicyclohexylcarbodiimide (DCC, ≥ 99%, Fluka), ethanol absolute (p.a, Aldrich), dichloromethane (DCM, ≥ 99.9%, Aldrich), methanol (≥ 99%, Fisher), N-methyl-2-pyrrolidone (NMP, ≥ 99.5%, Aldrich), toluene (≥ 99.5%, Aldrich), N,N-dimethylacetamide (DMAc, ≥ 99.8%, Aldrich), hydrochloric acid (36.5-38.0%, Alfa Aesar), copper(II) sulfate pentahydrate (98-102%, Fisher) and iron(III) chloride hexahydrate (≥ 98%, Sigma-Aldrich) were used as received. Poly(ethylene glycol) 3000, 6000, 10000, 35000 and 100000 were purchased from Sigma-Aldrich.

Synthesis of α,ω -dihydroxy-terminated Polysulfone (HO-PSU-OH)

Dihydroxy-terminated PSU polymers were synthesized by condensation of bis(4-chlorophenyl) sulfone (DCDPS) with an excess of bisphenol A calculated with the Carothers equation according to the literature procedure^{29, 33, 40, 74}. BPA (20 g, 87.6 mmol), DCDPS (24.4 g, 85 mmol), K₂CO₃ (36.32 g, 26.3 mmol), NMP (75 mL) and toluene (25 mL) were placed in a 250 mL three-neck round bottom flask equipped with a mechanical stirrer, a condenser, a thermometer, a Dean-Stark trap and a nitrogen inlet/outlet. K₂CO₃ was employed as a base, to generate the phenoxide ion of BPA in situ, which subsequently reacted with DCDPS at higher temperature. The reaction mixture was stirred at room temperature under nitrogen protection for 2 h to dissolve the reactants and gradually heated to reflux at 152 °C for 8 h to dehydrate completely via azeotropic distillation with toluene. Then, the toluene was distilled thoroughly at 160 °C. The reaction mixture was heated to 175°C for 8 h to start polymerization until the solution became too viscous. After cooling, the viscous mixture was precipitated into aqueous HCl/methanol (v/v = 2:1) with vigorous stirring in order to remove salts (KCl). The obtained polymer was dissolved in THF and reprecipitated into aqueous HCl/methanol trice, followed by filtration, then washing in water at 80 °C for 4 h to remove the remaining salts and solvents. After final filtration, the polymer was dried under vacuum at 90 °C for 24 h.

Synthesis of RAFT CTA-terminated Polysulfone (CTA-PSU-CTA)

RAFT chain transfer agent-capped polysulfone was synthesized through the Steglich esterification.³⁴ HO-PSU_{14k}-OH (20 g, 1.4 mmol, $M_{n, GPC}$ = 14 kg/mol, PDI = 2.1) was dissolved with 150 mL dry dichloromethane in 250 mL three-neck round bottom flask equipped with a magnetic stirrer, a condenser and a gas inlet/outlet.

[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (1.7 g, 4.3 mmol) and 4-(dimethylamino)pyridine (52 mg, 0.4 mmol) were added to the flask. The solution was stirred at 0 °C under nitrogen flow for 3 h. Then a solution of N,N'-dicyclohexylcarbodiimide (0.9 g, 4.3 mmol) dispersed in small amount of dichloromethane was added dropwise to the mixture. Subsequently the temperature was allowed to rise to room temperature and the reaction was continued under stirring for 3 days. The solution was filtered to remove catalyst and concentrated by rotavapor, followed by precipitation into methanol. The crude product was dissolved in dichloromethane again and reprecipitated into methanol (3 times), finally filtrated and dried in vacuum at 60 °C to obtain CTA-terminated polysulfone.

Synthesis of PtBA-PSU-PtBA Triblock Copolymer

The RAFT polymerization of PtBA-PSU-PtBA was carried out using CTA-PSU_{14k}-CTA as macro chain transfer agent and *tert*-butyl acrylate as monomer in DMAc at 80 °C, as follows: CTA-PSU-CTA (5 g, 0.3 mmol) was first dissolved with anhydrous DMAc (20 mL) in 100 mL of dry schlenk flask equipped with a magnetic stirrer. Next, AIBN (20 mg, 0.1 mmol) and tBA (30 mL, 0.2 mol) were added quickly, before the flask was sealed with a rubber septum, and then the reaction mixture was degassed by three freeze-pump-thaw cycles to switch the atmosphere to nitrogen. Finally, the schlenk flask with the reaction mixture was placed in a thermostatic bath at 80 °C for 24 h. After the reaction mixture was stopped by exposure of the solution to air and cooled down to room temperature, it was precipitated into water. The precipitate was recovered by filtration, washed with methanol and dried in vacuum. The polymer was solubilized with DMAc and reprecipitated into water. The purification step was repeated three times. After drying under reduced pressure, the triblock copolymer PtBA_{30k}-PSU_{14k}-PtBA_{30k} was obtained as yellowish solids.

Polymer Characterization

¹H and ¹³C NMR spectra of polymers were recorded with a Bruker AVANCE-III spectrometer at a frequency of 400 MHz at room temperature and deuterated solvents containing tetramethylsilane Si(CH₃)₄ as an internal standard. Polymer molecular weight and distribution were determined by triple detection gel permeation chromatography (GPC) from Viscotek using a GPCmax module (model VE-2001) and a GPC-TDA 305 system equipped with two columns (LT4000L, Mixed, Low Org. 300 mm X 8.0 mm) eluted at 1.0 mL min⁻¹ in stabilized THF at 35 °C. Three detectors are light scattering (RALS and LALS), refractive index, and viscometer. Absolute molecular weights were determined using polystyrene standards for calibration. Thermogravimetric analysis (TGA) was conducted using a TGA Q50 (TA instruments) with a heating rate of 10 °C min⁻¹ under nitrogen flow from 25 to 800 °C. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC 204 F1 NETZSCH under nitrogen flow. The heating rate was 10 °C min⁻¹ and the cooling rate was 5 °C min⁻¹ in the range of temperature from -50 to 180 °C. The glass

transition temperature (T_g) was taken from the second heating scan.

Membrane Fabrication

The casting solution from 20 wt % PtBA_{30k}-PSU_{14k}-PtBA_{30k} in DMAc was stirred for 12 h to obtain a homogeneous solution and kept still for another 12 h to release bubbles. This viscous solution was cast onto a clean glass plate by a doctor blade with 200 μ m gate height. The plate was then immersed quickly and smoothly into the coagulation bath of deionized water at room temperature. An opaque film formed and left the plate in a few minutes spontaneously. Then the membrane was transferred to a fresh water bath for exhaustive extraction of solvent overnight. The resulting membrane was stored in water at 4 °C before ultrafiltration experiment and surface modification. Some part of the membrane was freeze-dried for various characterization.

Computational Modeling of BAB Copolymer Self-Assembly

We model self-assembly of BAB block copolymer using a meso-scale method Dissipative Particle Dynamics (DPD).^{75, 76} The simulations use an open-source software Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).⁷⁷ These simulations use the standard DPD units⁷⁸ of length ($r_e = 1$), mass ($m = 1$), energy ($\epsilon = k_B T = 1$), and time ($\tau = 1$). We discretize each triblock copolymer chain with 148 particles, connected with spring potentials with an equilibrium bond length $r_{eq} = 0.8r_e$ and spring constant $K_s = 50 k_B T$. We impose periodic boundary conditions in cubic simulation boxes of size $L = 111.34r_e$. The box size is defined to be approximately 12-fold the unperturbed radius of gyration ($L \sim 12R_g$).⁷⁹ The particle-number density in all the simulations is $\rho_n = 3$ particles/ r_e^3 . The simulations evolve for 1 million of time steps, using a time step 0.04τ to ensure a proper control of the temperature of the system. The visualization of the computational results uses the software OVITO.⁸⁰ Detailed parameters definition and descriptions of the simulation method are provided in the Supplementary Information.

Membrane Modification

The as-formed PtBA-PSU-PtBA membrane was immersed into 37% hydrochloric acid (HCl) solution for 30 minutes with gentle swirling to partially cleave the tert-butyl groups to yield carboxylic acid functions. After hydrolysis in the HCl bath, the membrane was immediately moved to a beaker with 0.1 M CuSO₄ or FeCl₃ solution. The metal salt solution was refreshed at least three times in order to wash away remaining acid. The membrane was allowed to sit in the solution for 24 h to achieve complete metal complexation with carboxylic acid. Finally excess uncomplexed metal ions were washed out by DI water.

Membrane Characterization

The surface and cross-section morphologies of the membranes were observed by field emission scanning electron microscopy

(FESEM) in a FEI Nova Nano SEM. For surface imaging, a small piece of membrane sample was mounted on a flat aluminum stub, fixed by aluminum conductive tapes. For cross-section, the membrane sample was freeze-fractured in liquid nitrogen, and mounted on a 90° aluminum stub vertically with tapes. The samples were sputter-coated with 2 nm Iridium nanoparticles to prevent electron charging using Quorum Q150T before imaging.

Cryo SEM experiments were carried out to examine the bulk structure of membrane casting solution. A PP2000T cryo transfer system (Quorum Technologies, UK) attached to a FEI Nova Nano FEG SEM was used for this purpose. Small amount of sample was transferred onto the opening of a rivet (2 mm in diameter) that was mounted onto an aluminum stub. The sample was frozen in liquid nitrogen and transferred under vacuum into a PP2000T cryo preparation chamber precooled at -180 °C. Frozen sample was sputter coated with 5 nm-thick platinum in an argon atmosphere at -150 °C. The top part of the frozen sample was hit with a knife precooled at -150 °C to produce the fractured planes. In order to reveal the detailed structure of fractured planes, the samples were sublimed at -90 °C and sputter coated with 2.5 nm-thick platinum in an argon atmosphere at -150 °C. The sample was then transferred to SEM cryo stage, held at -130 °C, and high quality SEM images were captured. The secondary electrons were captured by the through the lens detector for imaging using accelerating voltages of 3-5 kV and working distance of 5 mm.

For transmission electron microscope (TEM), the membranes were embedded in epoxy and polymerized for 16 h at 60 °C. The PtBA-PSU-PtBA membrane was stained with RuO₄ vapor for 4 hours before embedding. Ultra-thin sectioning was performed using a Leica EM UC6. 100 nm thin sections were examined using a Titan G2 TEM operating at 300 kV (FEI company) equipped with a 4 k × 4 k CCD camera and an energy filter model GIF Tridiem (Gatan, Inc.). Electron energy loss spectroscopy (EELS) signal from the Cu L edge (Cu-L edge of 931 eV) and Iron (Fe-L edge of 721 eV) were acquired in energy-filtered TEM (EFTEM) mode for the distribution of Cu and Fe phases in the samples. Each elemental map was created by using a 3-window method.

The pore size distribution was evaluated by capillary flow porometry was measured in a POROLUXTM 1000 porometer. Porefill (16 mN m⁻¹) was used as the wetting liquid, which was displaced by nitrogen gas flow with the pressure up to 34.5 bar.

Dynamic mechanical analysis (DMA) experiments of the membrane films were performed using a TA Instruments DMA Q800. A piece of rectangular membrane was fixed by tension (film) clamps and tested under stress/strain controlled force mode with a force ramp rate of 0.1 N min⁻¹.

Contact angle measurement was performed on a Kruss Easydrop equipment in static mode at ambient temperature with 1 μ L water drop size. Each reported contact angle is the average of three measurements.

Ultrafiltration Experiments

Ultrafiltration experiments were conducted using a dead-end magnetically stirred homemade stainless steel cell with an effective membrane area of 1.04 cm² to evaluate the membrane performance. The membrane was precompactd by deionized water for 30 min at operation pressure of 1 bar. The stable pure water permeance J_w was calculated by using the following equation,

$$J_w = V / t S \Delta P \quad (4)$$

where V and t are the volume of the permeate and the time to collect it, respectively; S is the effective membrane area; ΔP is the transmembrane pressure. Afterwards the feed solution was replaced by a total of 0.5 wt% poly(ethylene glycol) mixture solution (0.1 wt % each of 3000, 6000, 10000, 35000, and 100000 g/mol). Samples of the feed solution and permeate were collected after the filtration test in the same manner. The rejection ratio of PEGs with different molar mass R, was calculated according to the equation,

$$R = (1 - C_p / C_f) \times 100 \% \quad (5)$$

where C_p and C_f are the PEG concentrations of each specific molecular weight in the permeate and feed solution, respectively. The concentration was measured by Agilent 1200 GPC using water as eluting solvent, two columns Agilent PL aquagel OH 60 μ m and Agilent PL aquagel OH 40 μ m. Molecular weight cut-off (MWCO) of the membranes was determined as the smallest molecular weight of PEG for which the membrane has more than 90 % rejection.

Antibacterial efficacy of the copper-containing cross-linked membrane

Pseudomonas aeruginosa PAO1 was used to evaluate the antibacterial efficacy. The methods and conditions were as described previously but with minor modifications.⁸¹ Briefly, *Pseudomonas aeruginosa* PAO1 was inoculated into 30 mL LB Broth (Lennox) (Sigma-Aldrich Co. LLC, St. Louis, MO, USA). After incubating for 24h at 37 °C, the bacterial culture was diluted with 0.85% w/v NaCl to an OD₆₀₀ of 0.07. This OD measurement at 600 nm wavelength corresponds to an approximate cell density of 10⁸ cells/mL. Prior to experiment, membranes were aseptically cut into 2 cm × 1.5 cm, and were respectively immersed into 10 mL diluted *Pseudomonas aeruginosa* PAO1 cell suspension. The cell suspensions were incubated in a 200 rpm shaker incubator at 37 °C for 24 h. After that, the membranes were removed from the cell suspensions with sterilized forceps and placed into individual tubes with 2 mL of 0.85% w/v NaCl. The tubes then were ultrasonicated for 3 min by a Q500 sonicator (Qsonica) at 25% amplitude to dislodge the attached bacteria into the suspension. This cell suspensions were diluted by 2000-fold with 0.85% w/v NaCl. LIVE/DEAD[®] BacLight[™] Bacterial Viability and Counting Kit (L13152) (Thermo Fisher Scientific Inc., America) was used to stain the bacteria based on manufacturer's protocol prior to live count cells by flow cytometry on Accuri C6 (BD Bioscience, NJ, USA). The attached bacterial cells on the membrane surfaces were also observed

by FESEM after fixing the cells with a 4% w/v paraformaldehyde solution.

Conclusions

We successfully synthesized for the first time poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) (PtBA-*b*-PSU-*b*-PtBA) copolymers. End-group modification, with trithiocarbonate RAFT agent on telechelic hydroxyl-terminated polysulfone from step-growth condensation, produced CTA-capped polysulfone for subsequent reversible-deactivation radical polymerization. This macro-CTA was further used in RAFT polymerization to obtain PtBA_{30k}-*b*-PSU_{14k}-*b*-PtBA_{30k}. The chemical structure of the triblock copolymer and precursors were verified by characteristic adsorption peaks in NMR and FTIR spectra. Thermal studies confirm the presence of PtBA blocks in the copolymer with characteristic weight loss at 220 °C measured by TGA and shift of T_g revealed by DSC. The GPC peak moved to the shorter retention time without any shoulder after the chain extension towards the triblock copolymer. This result strongly suggests RAFT polymerization was carried out in a controlled manner, which led to a narrowing of molar mass distribution from 2.1 to 1.4. The relatively low PDI allows the as-synthesized triblock copolymers to assemble into worm-like cylindrical micelles in DMAc. This self-assembly process was observed from solution cryo-FESEM micrograph. Based on Hansen solubility parameter, we propose a "flower-like" BAB arrangement with the PSU central block as the shell protecting the less solvated PtBA segments. The high polymer concentration, low composition of PSU, and highly swelled micelle cores are important factors in forming the specific micelle morphology as supported by our computational models. Once the same solution was cast and immersed into water, the worm-like cylindrical micelles on the surface were frozen, giving rise to the nanostructured membrane with a highly porous interconnected skin layer on top of graded finger-like macrovoids which are present in the lower portion. This asymmetric nanostructured membrane formed *via* SNIPS has high pure water permeance of 555 L m⁻² h⁻¹ bar⁻¹ with molecular weight cut-off of 28 kg mol⁻¹ compared to the normal phase inversion membranes. The combination of soft PtBA and rigid PSU blocks makes its mechanical strength comparable to commercial homopolymer membranes. A membrane surface modification method was proposed to obtain metal-containing cross-linked membranes by hydrolysis of PtBA and complexation with transition metals. The characterization of copper and iron-chelated membranes demonstrates that the surface morphology, water flux and MWCO could be successfully tuned by this modification. The copper-containing membrane shows improved antibacterial efficacy. With these properties, we propose their application as low fouling, solvent resistant and catalytic membranes.

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