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Membranes Prepared by Self-assembly and Chelation Assisted Phase Inversion

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We combine self-assembly in solution, complexation with metallic salts and phase separation induced by solvent-non-solvent exchange to prepare nanostructured membranes for separation in the nanofiltration range. The method was applied to synthesized poly(acrylic acid)-*b*-polysulfone-*b*-poly(acrylic acid) copolymers dissolved in a selective solvent mixture and immersed in aqueous Cu²⁺ or Ag⁺ solutions.

Biological systems have been long source of inspiration for synthetic membranes.^{1–3} Water channel proteins across cell membranes, Aquaporins, are a frequent example of high efficiency of water transport in biological cells.⁴ Innovative efforts on incorporating Aquaporin into lipid-bilayer-like block copolymer vesicles,⁵ or into impermeable membrane matrix have been reported.^{6,7} However, the robustness and scalability of aquaporin-based biomimetic membranes still remain a challenge towards practical application. Different approaches are under investigation to construct fully artificial water channel membranes as synthetic analogs of biological transport. Aligned carbon nanotubes are one of those.^{8–11} Nanochannels originated from assembled molecules have been reported by different groups: (1) helical channels from zwitterionic polymers coordinated with zinc,¹² (2) self-assembled cylindrical pores from dendritic dipeptide *via* peripheral π -stacking,¹³ (3) imidazole I-quartet superstructures stabilized by inner dipolar water wires,¹⁴ (4) organic nanotubes through the co-assembly of cyclic peptide and block copolymers,¹⁵ (5) single-molecular water channels formed from the hydrazide¹⁶ and peptide-appended pillar[5]arenes,¹⁷ and (6) well-defined nanotubes from shape-persistent macrocycles multiple hydrogen bonding and π -stacking.¹⁸ Until now most of the organic artificial water channels have permeabilities, which are a few orders of magnitude lower than biological analogues. Reliable tests have been mostly conducted in conditions far from practical membranes.²

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Nanostructured block copolymer membranes resemble in many aspects the self-assembly of natural biomacromolecules and have been subject of growing interest.³ When prepared by phase inversion induced by immersion in non-solvents, mesopores larger than 10 nm are formed.^{19–21} Pore reduction to nanofiltration (NF) range has been recently achieved by blending copolymers.²² Most reports are based on polystyrene (PS) blocks.

We aimed to fabricate water channel-containing membranes from a newly synthesized amphiphilic polysulfone-based triblock copolymer, poly(acrylic acid)-*b*-polysulfone-*b*-poly(acrylic acid) (PAA_{17k}-PSU_{14k}-PAA_{17k}). Polysulfone (homopolymer) is a high

Figure 1. (a) TEM images of PAA-PSU-PAA micelles from 0.1 wt% THF solution and (b) hydrodynamic size distribution determined by DLS; (c) FESEM image of PAA-PSU-PAA thin film spin-coated on silicon wafer; (d) topographic AFM image of PAA-PSU-PAA thin film after thermal annealing, and corresponding (e) phase image; (f) TEM image of cross-section of annealed PAA-PSU-PAA bulk, stained by RuO₄.

Scheme 1. Synthesis route of poly(acrylic acid)-b-polysulfone-b-poly(acrylic acid).

performance engineering resin and better accepted than PS as membrane material.²³ The preparation of amphiphilic copolymers with polysulfone blocks allows us to combine high stability and ordered self-assembled nanostructures. In addition here we propose the use of metal chelation to guide the self-assembly and promote physical crosslinking, leading to ordered permeation channels.

The PAA_{17k}-PSU_{14k}-PAA_{17k} copolymer was obtained by fully hydrolyzing a polymer precursor, PtBA-PSU-PtBA, which we recently reported,²⁴ with trifluoroacetic acid (TFA) in anhydrous dichloromethane (DCM),²⁵⁻²⁷ as depicted in Scheme 1. The detailed synthesis protocol, and the thermal and chemical characterization are provided as supporting information.

Spherical micelles with ~30 nm diameter in clusters of 0.5–1.0 μm were formed in 0.1 wt% solution in THF, as shown by transmission electron microscopy (TEM) in Figure 1a. The dynamic light scattering (DLS) results in Figure 1b confirmed a bimodal distribution of micelles with 25 ± 2 nm Z-average diameter and clusters of size up to 1000 nm. Table 1S shows that all contributions to the Hansen solubility parameter (δ) for THF are closer to PSU than to PAA.²⁸ PSU blocks are expected to constitute the micelle corona in the form of loops, shielding the PAA core from contact with THF. Highly solvated PSU coronas can associate with those of neighboring micelles to bridge them, forming larger agglomerates.²⁹⁻³¹

By spin-coating a 3 wt% copolymer solution in THF, worm-like structures are formed, as shown by FESEM (Field Emission Scanning Electron Microscopy) in Figure 1c. The morphological transition from spherical micelles in dilute solution (0.1 wt%) to elongated micelles follows the balance of enthalpic and competing entropic contributions, analogous to observed in other systems.³²

Thermal annealing at 180 °C in a vacuum oven erased the original elongated surface morphology, and led to nanoscale smoothness confirmed by FESEM (Figure S6), and topographic (height) Atomic Force Microscopy (AFM) images (Figure 1d, roughness ($R_a = 0.5$ nm)). AFM phase imaging³³ clearly indicates 50 nm domains dispersed in a continuous phase (Figure 1e). The domains are the soft PAA phase with lower viscoelasticity than the stiff PSU with a higher Young's modulus of 2.5–2.6 GPa.^{34, 35} Grazing-Incidence Small-Angle Scattering (GISAXS) of the thin film reveals a d-spacing of 41 nm, corresponding to the average distance between the center of the repeating domains (Figure S7). Figure 1f exhibits the film cross-section TEM image with PSU domains selectively stained by RuO₄ vapor³⁶ aligned to form channels.

We have demonstrated that the rational design of the selective solvent mixture plays a decisive role in the morphology of block copolymer membranes prepared by phase inversion.^{37, 38} In order to

Figure 2. (a) TEM image of PAA-PSU-PAA micelles from 0.1 wt% DMF/THF/acetone solution (10/45/45) stained by uranyl acetate and (b) hydrodynamic size distribution determined by DLS; (c) Surface, (e) cross-sectional FESEM images and (f) TEM image of PAA-PSU-PAA membrane prepared from 20 wt% polymer solution in DMF/THF/acetone mixture with 0.1 M CuSO₄ and (d, FESEM) 0.1 M AgNO₃ bath; insets in c and d: photographs of the corresponding membranes; (g) supramolecular micelle arrangement with PSU (brown) core and PAA (blue) corona in membranes.

obtain a spherical micelle structure with hydrophilic PAA segments forming the corona, we proposed a tertiary solvent system composed of DMF, THF and acetone in a ratio of 10/45/45. THF solubilizes both PAA and PSU blocks, but favors a PSU corona. To reverse this arrangement, an equal amount of acetone was added to the mixture. Acetone solubilizes PAA but just swells PSU homopolymers. Its H-bond contribution to δ and dielectric constant ϵ lie between those of THF and DMF (Table 1S). It hinders the complete ionization of PAA and reduces the repulsion between PAA

segments. The corona becomes more compact and less deformable. DMF was added as common solvent (stronger affinity for PAA) to achieve a homogeneous solution.³⁹

Figure 2a shows the TEM image of micelles from a dilute solution (0.1 wt%) in the ternary solvent system. PAA formed the spherical corona, since the outer shell is darker after staining with uranyl acetate.⁴⁷ The main peak of the DLS histogram corresponds to a Z-average hydrodynamic diameter of 115 ± 2 nm (Figure 2b). The presence of small particles below 10 nm suggests that some free unassociated polymer chains coexisted in the solution.

Membranes were prepared by casting concentrated triblock copolymer solutions (20 wt%) in the ternary solvent mixture on polyester nonwoven, allowing evaporation for 5 min and immersing into water. A rough membrane surface was formed (Figure S8), due to excessive swelling of the PAA block in water. To stabilize the membranes an additional step of physical crosslinking is required. Phillip et al. first reported nanostructured PS-based block copolymer membranes with PAA-lined pores, tested for selective metal adsorption.⁴⁰ Here we used metal complexation as a tool for self-assembly stabilization during the membrane formation. In a previous work, we proposed a two-step surface modification for PtBA-PSU-PtBA membrane, in which the membrane is partially hydrolyzed with acid and then exposed to metal ions for physical crosslinking.²⁴ By adding CuSO_4 or AgNO_3 to the coagulation bath, a membrane was produced, with mechanical strength suitable for practical filtration. Due to the combination of two processes, we referred the method as self-assembly and chelation assisted non-solvent induced phase separation (SCNIPS). The final micelle arrangement in membranes is illustrated in Figure 2g. Aggregated PAA domain between PSU cores serves as nanopores.

The as-formed membranes display the characteristic colors of the chelated metal ions, blue for membrane formed in a 0.1 M CuSO_4 bath and yellowish for that formed in 0.1 M AgNO_3 , as shown in the insets of Figure 2c and d, respectively. The FESEM and TEM images in Figure 2c and 2f and suggest that densely packed spherical micelles are formed in solution and stabilized by immersion in the Cu^{2+} coagulation bath, as depicted in Figure 2g. The thickness of this dense film is about 10 microns (Figure 2e).

Metal chelation helped to promote the solidification of membranes and increased the micelle-micelle interconnectivity, preserving their morphology in the final membranes. The copper in the membrane could be removed by 0.1 M HCl aqueous solution, which protonated PAA and broke the complexation. FESEM image (Figure S9) of this membrane after metal removal shows a porous membrane without particular order, similar to that of the membrane formed in pure water bath (Figure S8).

The membrane morphology features water-permeating PAA channels. Filtration experiments show that the Cu^{2+} membrane has a pure water permeance of $0.15 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is lower than that of the commercial RO membranes because the selective film prepared here is much thicker. The sodium chloride rejection of this membrane is 21 %. To reduce the membrane thickness, we dip-coated 3 wt% copolymer solutions in THF on polyacrylonitrile (PAN) porous support, followed by evaporation and immersion in CuSO_4 bath. FESEM and TEM images in Figure S10 confirm a thin copolymer selective layer (less than $0.5 \mu\text{m}$) with the same water-channel structure, formed on top of the PAN support. Due to the thinner selective layer, the pure water permeance increases to $1.65 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, with the NaCl rejection increasing to 42 %, indicating that the dip-coating leads to a surface layer with less defects than the previous approach. In comparison to NaCl, this charged

membrane rejects 83% magnesium chloride (MgCl_2), a salt with multivalent cation. This can be explained by the Donnan exclusion theory for nanofiltration membranes.⁴¹ In the neutral feed solution, the positive acid groups in PAA repel the co-ion, Mg^{2+} more strongly than Na^+ due to the charge effect. This result is consistent with the trend in ion rejection of charge-functionalized membranes reported by Qu et al.⁴² The channel size of the membrane was estimated using rejection measurements of poly(ethylene glycol) (PEG) as neutral solutes. The membrane has a molecular weight cut-off of 7000 g/mol, corresponding to a mean pore size of 2.3 nm (Figure S11).

The stability of the membrane was investigated, by measuring the copper concentration in the permeate, using inductively coupled plasma optical emission spectrometry (ICP-OES). Feed solutions of pure water and 10 g/L MgCl_2 solution were used. The copper content observed in all permeates collected at 4 h and 29 h filtration was less than 10 ppb, indicating that no significant leaching occurs during filtration and copper is strongly complexed with the copolymer.

The proposed technique is a one-step method to prepare membranes complexed with high loading of metal ions, which could be used as functional materials for a variety of applications. The silver-containing membrane is of particular interest because the incorporated Ag^+ can be readily reduced to Ag^0 nanoparticles immobilized in the membrane matrix.^{43,44} Once the PAA-PSU-PAA membrane formed by immersion in AgNO_3 aqueous solution was transferred to a 0.2 mM NaBH_4 solution, its surface immediately became dark yellow and a few minutes later shiny silver (Figure S12b). The surface of the obtained membrane is fully covered with silver nanoparticles with a grain size of around 100 nm, as indicated by FESEM in Figure S12a. By analyzing the TEM image of the membrane, we can easily identify three distinct layers (Figure S12c). Underneath the 150 nm thick top layer, consisting of large Ag^0 nanoparticles, there is a sublayer of 500 nm thickness, in which smaller nanoparticles with a diameter of ~ 20 nm are densely packed, as shown in Figure S12d. Nanoparticles were not detected below this layer. Figure S12e confirms that only the micellar morphology expected for the pristine membrane, prepared with Ag^+ bath, was observed in areas far from the surface, indicating that NaBH_4 might not further penetrate to effectively reduce silver.

In summary, poly(acrylic acid)-*b*-polysulfone-*b*-poly(acrylic acid) ($\text{PAA}_{17k}\text{-PSU}_{14k}\text{-PAA}_{17k}$) triblock copolymers were successfully synthesized by hydrolyzing poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) and promoting metal complexation with the PAA blocks. Metal ions in coagulation bath can preserve the morphology of large spherical micelles containing PAA corona, assembled in casting solutions with a selective solvent mixture DMF/THF/acetone (10/45/45). By dip-coating the copolymer solution on PAN supports, thinner selective layers with higher water flux and better salt rejection were obtained. The ordered space between micelles filled with PAA act as preferential water channel. Reduced metallic nanoparticles were obtained. The incorporation of nanoparticles in the membrane opens the door to more applications such as catalytic and anti-bacterial materials.

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