Double Stimuli-Responsive Porous Membranes from Polystyrene-block-poly(N,N-dimethyl-aminoethyl methacrylate) Diblock Copolymers

Felix Schacher¹, Tobias Rudolph¹, Mathias Ulbricht², and Axel H. E. Müller¹

¹Makromolekulare Chemie II and Zentrum für Kolloide und Grenzflächen; Bayreuth University, D-95440 Bayreuth, Germany; E-mail: axel.mueller@uni-bayreuth.de
²Technische Chemie II, Universität Duisburg-Essen, D-45117 Essen, Germany

INTRODUCTION

Block copolymers represent an ambitious class of materials as their scope of applicability is still rising. Mostly, this is due to their imitable self-assembling properties, rendering them suitable for applications in solution, in thin films or as components of porous composite membranes. Also in the field of industrially important membrane production processes, in particular via controlled phase separation (“phase-inversion”) of polymer solutions, block copolymers are becoming more and more popular. This is mainly attributed to the constantly increasing number of processes in which the desired separation problem cannot be solved with state-of-the-art membranes. One of the key features of block copolymers is the facile implementation of “smart” materials, containing compartments with the ability to change conformation or properties upon application of environmental stimuli like pH, temperature or light. Non-solvent-induced phase separation (NIPS) is the most important industrial process for the fabrication of “asymmetric” membranes, having a very thin “skin” layer supported by a macroporous substructure. Recently, this process has been applied for the first time to well-defined block copolymers, polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP). However, the reported procedures yield membranes which can react to a single stimulus only.

Here we present the formation of double stimuli-responsive porous membranes for the possible applications in ultrafiltration or microfiltration. These materials combine a rather narrow pore-size distribution with mechanical stability and high water flux. The membranes were prepared via NIPS from amphiphilic polystyrene-block-poly(N,N-dimethylaminoethyl methacrylate) (PS-b-PDMAEMA) diblock copolymers in THF/DMF mixtures. The resulting structures are self-supporting and defect-free over several hundred µm. The advantage of using PDMAEMA as the hydrophilic block is that its solubility in aqueous solution can be triggered by two stimuli, pH and temperature.

EXPERIMENTAL

Sequential Living Anionic Polymerization in THF. Polystyrene-block-poly(2-dimethylaminoethyl methacrylate) was synthesized via sequential living anionic polymerization in THF (500 ml) at low temperatures. First, styrene was initiated with sec-butyllithium at −70°C and polymerized for 30 minutes. For polymerization of the second block, the polystyrene chains were end-capped with 1,1-diphenyl ethylene at −50°C in order to attenuate the reactivity of the anions. DMAEMA was injected via syringe into the reaction vessel and was polymerized for 1 h at −40°C. Finally, the reaction was stopped through addition of 3 ml of degassed isopropanol, and the polymer precipitated in water.

Membrane Preparation. Membranes were prepared via the NIPS process. 200 µm thick films were cast from a solution of PS-b-PDMAEMA (1.5 g, 15 wt. %), DMF (4.25 g, 42.5 wt. %) and THF (4.25 g, 42.5 wt. %) with a doctor blade onto polished glass substrates. After 60 seconds exposure to air (relative humidity was 30-40%) and temperature at ~20°C, the as-cast films were immersed into a bath containing de-ionized water for final formation of the membrane morphology. During the next 60 minutes, the films started to lift off the glass surface. After 12 hours, the membranes were taken out of the water bath, stored in de-ionized water until used and characterized as follows.

Water Flux Measurements. Water flux measurements were carried out in a stirred ultrafiltration test cell (Amicon 8010, Millipore, effective membrane diameter 22 mm) connected to a water reservoir at a constant height of the water column of 25 cm, providing a transmembrane pressure of 0.025 bar. pH was adjusted through dilute solutions of NaOH and HCl in deionized water. Temperature ramps were performed through keeping the whole ultrafiltration cell in a tempered water bath. Steps were 10 K, equilibration time in between two points was 1 hour, except for the highest temperature (65°C: 2 hours).

Filtration of Silica Particles. Filtrations of colloidal silica particles were carried out with the same ultrafiltration cell as described above, but at a pressure of 0.1 – 0.2 bar supplied by compressed nitrogen. The feed solutions were prepared through diluting the particle stock solutions with de-ionized water and adjusting the pH with NaOH or HCl. Typically, 10 ml of the feed solutions were filled into the Amicon cell. After the filtration of 8 ml, the remaining 2 ml were kept as retentate solution. Upon changing the particle size, the cell was rinsed 5 times with de-ionized water, and afterwards 50 ml water was passed through the membrane to remove adsorbed silica particles.

Dynamic Light Scattering. Dynamic light scattering (DLS) measurements were performed in sealed cylindrical scattering cells (d = 10 mm) at a scattering angle of 90° on an ALV DLS/LSL-SP 502F equipment consisting of an ALV-SP 125 laser goniometer with an ALV 5000/E correlator and a He-Ne laser with the wavelength λ = 632.8 nm. The CONTIN algorithm was applied to analyze the obtained correlation functions. Apparent hydrodynamic radii were calculated according to the Stokes-Einstein equation.

RESULTS

The final composition of the diblock copolymer was determined as PS₈₁PDMAEMA₁₉⁻⁻. The subscripts denote the weight fractions in % and the superscript the molecular weight in kg/mol.

The NIPS process is a straightforward and fast one-step procedure. Membranes formed by this preparation process usually exhibit an integrally anisotropic cross-section and are classical examples for high-performance materials for pressure-driven separation processes like ultrafiltration, nanofiltration or reverse osmosis. An intrinsic feature is the thin separation layer on top (thickness ~50 nm up to several µm), supported from underneath through the main macroporous part of the membrane. We used a mixture of THF (50%) as a highly volatile solvent with DMF (50%). Polymer concentration was 15 wt. %. After immersion in the precipitation bath, final solvent exchange and solid film formation take place. The membranes were taken out of the water bath after 12 hours and dried in vacuum for scanning electron microscopy (SEM) analysis (Figure 1).

Figure 1. Cross-sectional SEM micrograph for a S₈₁D₁₉ asymmetric membrane, scalebar corresponds to 1 µm.

Figure 1 shows a cross-section of the asymmetric membrane. Clearly, a distinguished separation layer is obtained on the top with a thickness of around 1 µm. Beneath this porous layer, broader channels appear with an evident arrangement perpendicular towards the former glass substrate. This cross-section structure is typical for polymer membranes obtained by NIPS with rapid precipitation.
During water flux measurements, environmental conditions were varied to trigger the two possible stimuli for PDMAEMA (Figure 2).

At pH 2 a viscosity-corrected flux value of 0.025 L/m² was obtained. No flux increase could be detected upon raising the temperature to 65 °C. This is due to full protonation of the PDMAEMA segments, keeping the charged polymer chains extended at all temperatures. At pH 6, PDMAEMA is still partially protonated (pKₐ = 7.78°). The measured flux at room temperature is not significantly high and does not change until 55°C. However, at 65 °C, flux increased by a factor of 4. Here, the charge density along the polymer chain segments is considerably lower than at pH 2, resulting in a certain collapse upon heating above the phase transition temperature. Though, some charge is present and hence the chains cannot completely collapse. Therefore, the transmembrane flux does not reach its maximum value. At pH 10 and 25 °C, the flux is already high. At this pH, the polymer chains are uncharged and less extended. At 65 °C the flux further increased, indicating a further collapse of the PDMAEMA segments. If the flux at pH 2 and 25 °C is compared to the final value at pH 10 and 65 °C, permeability increases by a factor of 7. Assuming standard pore flow models, this corresponds to a change in effective pore radius by a factor of 2 to 3.

To evaluate the actual pore size distribution of the membranes filtration experiments with synthetic silica colloids at different pH-values were carried out. To minimize adsorption to the membrane, the concentrations were kept low (0.1 – 0.2 %) in all cases. Retention was determined by the comparison of the count rate obtained via dynamic light scattering (DLS) for feed, retentate and permeate solutions. Silica colloids with 22, 36, 60, and 104 nm diameter were filtered at pH 6 and pH 10. The results are shown in Figure 3.

At pH 6, some silica colloids were rejected, but not fully. The amount of rejected particles in this case was measured to be 37 %. This can be explained by the collapse of the PDMAEMA chains under these conditions. Thus, the membrane pores are more "opened", enabling a significantly less hindered permeation of the 22 nm silica particles through the pore channels.

CONCLUSION

We successfully prepared double stimuli-responsive porous membranes via the non-solvent induced phase separation method from an amphiphilic diblock copolymer. The structures exhibit a thin separation layer with barrier pores in the range of ~10-30 nm and a thickness of around 1 µm. Both stimuli could be reversibly applied. The inherent features of these membranes besides two independently executable switches are constant and reproducible flux values, absence of noticeable defects on a scale of several hundred µm² and their ability to form self-supported mechanically stable films. The novel functional materials are ultrafiltration membranes with tunable cut-off pore size. It will now be the subject of further investigations to evaluate the usefulness of these novel materials in areas like the filtration or removal of viruses, bacteria and other particles.

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