



# Advanced ultrafiltration membranes by leveraging microphase separation in macrophase separation of amphiphilic polysulfone block copolymers

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## ABSTRACT

Water-soluble polymers are generally required in the process of nonsolvent-induced phase separation (NIPS) as additives or modifiers to enhance the hydrophilicity and permeability of ultrafiltration membranes. In this work, we demonstrate that amphiphilic block copolymers, polysulfone-*block*-poly (ethyleneglycol) (PSf-*b*-PEG), dissolved alone in solvents without any additives lead to highly permeable, fouling-resistant membranes via the NIPS process. PEG blocks deliver dual functions in the membranes. Selective enrichment of PEG blocks on the membrane surface as a result of surface segregation enhances the hydrophilicity and consequently fouling resistance of the membranes. Moreover, microscale phase separation of the block copolymers drives the formation of interconnected PEG microdomains distributed throughout the bulk membrane as confirmed by the transmission electron microscopy analysis on stained membrane slices. PEG microdomains serve as water channels facilitating water transport through the membrane. As a result, thus produced membranes exhibit excellent permeability a few times higher than other PSf-based ultrafiltration membranes with similar retentions. For instance, a membrane having the molecular weight cut-off of 70 kDa gives a water permeability as high as  $450 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . Furthermore, the retentions of the PSf-*b*-PEG membranes can be tuned in a relatively wide range simply by adjusting the copolymer concentration in the casting solutions. Using amphiphilic block copolymers alone as the base materials for the preparation of ultrafiltration membranes by NIPS not only simplifies membrane manufacturing process but also opens a new avenue to prepare advanced membranes with upgraded permeability and fouling resistance.

## 1. Introduction

Membrane-based water treatment requires membranes having good hydrophilicity [1–4] to allow water penetration and to alleviate the deposition of foulants. However, most membranes are prepared from polymers which are highly hydrophobic in nature, for example, polysulfone (PSf), polyvinylidene fluoride (PVDF), polypropylene (PP), etc. To enhance the membrane hydrophilicity and fouling resistance, amphiphilic copolymers which are composed of both hydrophilic and hydrophobic chains are frequently incorporated into casting solutions as additives or modifiers for the preparation of microfiltration or ultrafiltration (UF) membranes via the process of nonsolvent-induced phase separation (NIPS) [5,6]. The principle for the use of the amphiphilic copolymers lies in that the hydrophobic segments are mixed with the membrane skeleton composed of the base polymers by chain entanglement whereas the hydrophilic ones are forced to segregate on the pore walls/membrane surface in the phase inversion process [7]. A long-standing surface hydrophilicity, and consequently

enhanced permeability and fouling resistance are therefore expected as the hydrophilic chains migrated on the surface are not easy to leach out in operations because they are covalently bonded to the hydrophobic parts. Of course, this requires that the hydrophobic parts in the copolymer additives have a good compatibility with the base polymers.

Amphiphilic copolymers with the hydrophilic and hydrophobic chains connected in the random [8], graft [9], and block [10–12] mode have been used for this purpose. For instance, triblock copolymers of hydrophilic polyethylene oxide (PEO) and hydrophobic polypropylene oxide (PPO) connected in the sequence of two end PEO blocks capping one PPO middle block, that is, PEO-*block*-PPO-*block*-PEO, are extensively used and are doped into the casting solutions of many different polymers and enhanced membrane wettability and fouling resistance are generally achieved [13,14]. However, the incorporation of the copolymer additives inevitably complicates the membrane manufacturing process, and even worse, it may unexpectedly change the phase separation process and possibly weaken membrane performances [15]. To minimize these issues, these copo-

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lymers are typically doped into the casting solutions with percentages less than 20% [8–14].

Very recently, we blended amphiphilic block copolymer (BCP), polysulfone-*block*-polyethylene glycol (PSf-*b*-PEG), with PSf base polymer at various percentages up to 70%. We observed no compatible issue between the homopolymer and block copolymer as they were miscible at any blend ratio. Thus-produced blend membranes exhibited greatly improved performances in terms of permeance, hydrophilicity and fouling resistance. In addition to the surface segregation effect of the PSf-*b*-PEG copolymers, such superior performances are believed to be contributed also by the additional water permeability through PEG microdomains [16]. In this previous work, the PSf-*b*-PEG block copolymer was used with percentages up to 70% and they should not be regarded as additives any longer and actually they also served as one of the membrane-forming base polymers [16]. However, the PSf homopolymer was still involved as the other base polymers.

In contrast to the extensive use of amphiphilic copolymers as additives along with membrane-forming base polymers, it is rarely reported for the use of these copolymers alone as the membrane-forming base polymers. Using amphiphilic copolymers alone as the base polymers in the NIPS process makes the recipes of the casting solutions extremely simple which contain only the copolymer and the solvent and other additive is not required anymore. Such a simple recipe strongly benefits the membrane manufacturing and promises stable control in membrane performances, which is strongly desired from the viewpoint of large-scale production. More importantly, in addition to the phase separation at the macroscale in the NIPS process, there is also the possibility of microscale phase separation between the hydrophilic chains and hydrophobic chains in the copolymers [17,18], providing new and additional measures to gear, and to improve the membrane performances. However, the commonly used copolymer additives are not suitable to be used as base polymers to produce membranes because of their poor mechanical stability and membrane-forming property as “materials”. For instance, the PEO-*block*-PPO-*block*-PEO copolymers which typically have a molecular weight lower than 20,000 Da do not have any mechanical strength and even worse, cannot be solidified from the solution through the typical NIPS process [19,20].

Considering that PSf-*b*-PEG block copolymers with various PEG volume fractions can be readily synthesized with good yields at affordable costs [21], the copolymers themselves may serve as a good candidate for the production of separation membranes if we appropriately choose the PEG content in the copolymers. In the present work, we lower down the PEG content in the PSf-*b*-PEG block copolymers to 21 wt% and the copolymers are expected to largely maintain the good mechanical strength and the membrane-forming property of the PSf homopolymer on one hand, and the presence of PEG in the copolymer may enhance the hydrophilicity and permeance of the membrane through the effect of both surface segregation and “water channel” effect of the PEG microdomains on the other. The novelty and significance of the current work are multiple, which include (1) it opens a new avenue to produce hydrophilic PSf membranes, which is highly important and demanded as PSf membranes are extensively used in a diversity of fields and the strong hydrophobicity of PSf is always a problem [22]; (2) it suggests a simplified process to produce advanced UF membranes in which additives are no longer required; (3) it solves the issues of incompatibility between the base polymer and the additives and the leaching out of the additives which frequently plague the traditional NIPS process where foreign additives are involved.

## 2. Experimental

### 2.1. Materials

The PSf-*b*-PEG block copolymer was provided by Nanjing

Bangding. According to the manufacturer, the PSf block has a molecular weight comparable to that of Solvay P3500 polysulfone, and the PEG block has a molecular weight of ~20 kDa. The weight ratio of the PEG block in the copolymer was determined to be 21% by thermogravimetry. PSf homopolymer (P3500) and PEG homopolymer (molecular weight=400 Da) were obtained from Solvay and Sigma, respectively. Reagent grade N-methyl-2-pyrrolidone (NMP, purchased from Sinochem Chemical Reagent Co.) was applied as the solvent to dissolve the copolymer. We selected deionized (DI) water as the only component of the nonsolvent in the coagulation bath. Bovine serum albumin (BSA) was purchased from Sigma-Aldrich and was dissolved in phosphate buffer solutions (PBS) to be used in the rejection and fouling resistance tests.

### 2.2. Preparation of PSf-*b*-PEG membranes

The casting solutions of five different ratios in weight (ranging from 14% to 18%) were prepared by dissolving varying quantities of PSf-*b*-PEG in NMP at 60 °C. It took several hours to ensure that the PSf-*b*-PEG was visually dissolved and then the solution of BCP was handled under mechanical stirring at room temperature for 4 h so that PSf-*b*-PEG was completely dissolved in NMP. We kept the casting solutions in vacuum oven overnight to remove air bubbles. Subsequently, the copolymer solution was cast onto a nonwoven with a casting knife to obtain a casting film of 220 μm thick. The cast film was allowed to stand in air for 10 s and then coagulated in DI water at room temperature. The prepared membranes were thoroughly washed with DI water and stored in water for use. Water was changed every other day to avoid the growth of microorganisms. To compare the fouling resistance, blend membranes of PSf and PEG homopolymers were also prepared. The two homopolymers were mixed together with 21 wt% PEG and were dissolved in NMP with the total polymer concentration of 15%, and the following process for the membrane preparation is identical to the preparation of PSf-*b*-PEG membranes.

### 2.3. Characterization

Scanning electron microscopy (SEM) investigations on samples sputter-coated with Au/Pd alloy were performed with a field emission SEM (Hitachi S4800) operated at 5 kV to observe the surface and cross-sectional morphology. Samples were fractured in liquid nitrogen to expose their cross sections for SEM observation. The X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 XPS system (Thermo Scientific) using a monochromatic Al K $\alpha$  X-ray source. To compensate the surface charge effects, all binding energies in the spectra were referenced to the C 1s neutral peak at 285.0 eV. Transmission electron microscopy (TEM) was used to probe the morphology of PEG microdomains in the membrane. The membrane was embedded in epoxy resin and microtomed by a diamond knife on a Leica EM UC7 microtoming system at room temperature after curing. Then thin slices with a thickness of ca. 70 nm were connected on holey carbon grids and stained by osmium tetroxide (OsO $_4$ ) at 30 °C for 12 h. TEM was conducted with a FEI Tecnai TF20 transmission electron microscope operated at 200 kV. Gel permeation chromatography (GPC, Waters 1515) was applied to measure the molecular weight cut-off (MWCO) of the membrane. A contact angle goniometer (Dropmeter A-100, Maist) was employed to obtain the water contact angles. For each sample, at least 10 sites were tested and the averaged water contact angle was reported.

Cloud points were determined by the titration of the casting solutions with a concentration of 15 wt% different polymers, including polysulfone homopolymer and PSf-*b*-PEG copolymer in NMP, to which non-solvent, DI water, was added. The volume of the polymer solution is 10 ml. The cloud point is defined as the added amount of DI water at which the liquid-liquid phase separation was visually observed and the precipitate did not redissolve at 60 °C within 6 h.

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