



Upgrading polysulfone ultrafiltration membranes by blending with amphiphilic block copolymers: Beyond surface segregation



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ABSTRACT

Surface segregation of amphiphilic copolymers in the phase inversion process has long been used to improve membrane hydrophilicity. Typically, the copolymer is sparsely dosed into the casting solutions as additives. Herein we substantially increase the dosages of amphiphilic copolymers, and obtain blend ultrafiltration membranes with synergetically upgraded performances because of extra permeability-enhancing effect of the copolymer in addition to the surface segregation effect. We blend amphiphilic block copolymer, polysulfone-*block*-polyethylene glycol (PSf-*b*-PEG), with polysulfone base polymer at various percentages up to 70%. There is no compatible issue between the PSf and PSf-*b*-PEG as they are miscible at any blend ratio. Infrared spectroscopy and X-ray photoelectron spectroscopy confirm the surface segregation of PEG blocks. Moreover, PSf-*b*-PEG evidently influences the phase separation process by slowing down the precipitation rate of the polymer solutions, thus producing membranes with thicker skin layers. Interestingly, increasing copolymer percentages result in more water-permeable PEG microdomains in the blend membranes and consequently enhanced water permeance. The blend membranes exhibit simultaneously upgraded permeance, hydrophilicity, fouling resistance, and also performance stability. The highest permeance reaches nearly 400 L/(m² h bar) at a copolymer percentage of 40%, which is much higher than those of PSf membranes prepared in other works. By comparing with PEG homopolymer, we identify that the superior performances are originated also from the additional water permeability through PEG microdomains in addition to the effect of surface segregation of PSf-*b*-PEG copolymers.

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1. Introduction

Polysulfone (PSf), as an engineering plastic with a glass transition temperature of nearly 200 °C, is one of the most extensively used polymers for membrane separations because of its superior thermal stability, mechanical robustness, chemical resistance, excellent processibility as well as convenience in tuning membrane microstructures [1]. Typically, PSf is manufactured into ultrafiltration (UF) membranes through the nonsolvent-induced phase inversion (NIPS) and thus-produced PSf membranes are usually used in aqueous circumstances including water treatment [2], protein purification and fractionation [3], hemodialysis [4] and reverse/forward osmosis (as the substrates for thin-film composites) [5]. However, as can be easily seen from the multiple aromatic rings and scarcity of polar groups in its molecule PSf is strongly hydrophobic in nature. Membranes produced purely from

neat PSf suffer from very limited permeability, poor fouling resistance, and shortened lifetimes [6]. Consequently, polar additives are frequently introduced into the casting solutions in the production of PSf membranes, or post modifications are used to improve their hydrophilicity [7].

A number of physical or chemical approaches has been used to enhance the hydrophilicity of PSf membranes [8], mainly including adding inorganic nanofillers into membrane matrix [9,10], plasma etching to generate polar groups on the surface [11] and directly grafting some hydrophilic groups onto the membranes surface [1,12–14]. Besides, using hydrophilic additives is most technically and commercially feasible since most PSf membranes are prepared by the NIPS process in which additives can be readily co-dissolved into the casting solutions [15]. The extra advantage of hydrophilic additives is improving the flux of water. It is believed that the pore size in the selective layer, porosity, and pore interconnection will be enlarged with the incorporation of hydrophilic additives into the membranes as the subtle interactions among polymer, solvent, and nonsolvent are changed with the presence of the additives [16].

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Water-soluble/dispersible polymeric additives, such as polyethylene glycol (PEG) or polyethylene oxide (PEO) (PEG and PEO share the same molecular backbone and thus close physico-chemical properties but they have different end groups as they are synthesized from different monomers) [17], polyvinylpyrrolidone (PVP) [18], polybenzimidazole (PBI) [19], and polyaniline (PANI) [20–22] are most frequently included into the recipes of PSf membranes. In this regard, PEG is of particular interest because of its strong hydration effect, biocompatibility, as well as easy availability with variable molecular weights [15,23–25]. Typically, higher percentages of polymeric additives lead to membranes with a stronger hydrophilicity and permeability. However, over-dosed additives may not be compatible with the casting solutions and ruin the phase inversion process as well as the membrane performances. An even worse situation for these hydrophilic additives, which are usually water-soluble, is that a large portion of them will leach out during the phase inversion process and the subsequent operations in aqueous circumstances, leading to decaying performances in terms of both hydrophilicity and permeability [16,26].

A solution to this leaching problem is to use amphiphilic copolymers containing both hydrophobic segments and hydrophilic segments. The hydrophobic parts are believed to be anchored to the membrane skeleton by chain entanglement and the hydrophilic ones are forced to segregate on the pore walls in the phase inversion process [27]. To this end, both graft and block copolymers (BCPs) have been used and enhanced hydrophilicity have been clearly evidenced in most cases although the improvement in water permeance was frequently not observed. For the specific case of PSf membranes discussed in the present work, in addition to usages of PEG or PEO homopolymers as additives where the loss of these additives are considered to be unavoidable [16], copolymers of PSf and PEG are expected to promise stable improvement of the membrane performances as the PSf components in the copolymer will be fully compatible and miscible with PSf homopolymers which are the base material for the membranes. Hancock et al. firstly used polysulfone-*block*-polyethylene oxide BCPs, PSf-*b*-PEO, as additives to create blend semipermeable membranes for medical purpose [28,29]. Several years later, Mayes and coworkers synthesized graft copolymers of PSf and PEG, PSf-*g*-PEG, and blended them into the PSf casting solutions to prepare PSf membranes [1]. In both cases, the enhanced hydrophilicity and the consequently improved resistance to protein adsorption were remarkable. However, both groups did not investigate the separation performances of the produced membranes. In addition, Zhu and coworkers also observed clearly enhanced hydrophilicity of PSf membranes by combining other PSf-based amphiphilic BCPs into the casting solutions. However, the contribution of the combining PSf copolymers on the membrane performances remained unelucidated as the role of PEG homopolymers used as co-additives in their work cannot be excluded [30].

Interestingly, in previous works amphiphilic copolymers were used “really” as additives or modifiers as they were dosed in the casting solutions with small percentages, typically less than 20 wt% in the total polymer concentrations [1,28–30]. This is a reasonable and practicable strategy if these copolymers are mechanically weak as materials, or poorly compatible with the base polymers, or costly in price. The small dosages of copolymers may still deliver the function to enhance the membrane hydrophilicity as surface segregation does not require large amount of additives. However, it remains open what will occur when the dosage of copolymers is increased be comparable to that of the base polymer given that affordable, mechanical strong copolymer is available. In this situation, the copolymer is not only the additive in the common sense as it is also a major component of the produced membranes which should be considered as blend membranes. The

copolymer blended in the membrane casting solutions with dosages comparable to that of the base polymer will significantly influence the phase diagram of the solutions. Therefore, it may offer us a new strategy to tune the membrane microstructures and performances in addition to the well-studied effect of surface segregation.

Considering that PSf-*b*-PEG BCPs can be conveniently synthesized with good yields and this copolymer largely maintains the good mechanical robustness of PSf homopolymers [1,28–30], in the present work, we blend PSf-*b*-PEG BCPs with PSf homopolymer at various percentages up to 70% to prepare blend UF membranes through the NIPS process. The surface segregation also occurs, leading to enhanced surface hydrophilicity. Furthermore, the heavily dosed BCPs substantially change the microstructures and separation performances of the PSf membranes by forming water-permeable PEG microdomains. As a consequence of the dual effect of the blended BCPs, the permeance, hydrophilicity, fouling resistance, and also the performance stability of the blend membranes are synergistically improved. Specifically, the blend membranes with 40% content of PSf-*b*-PEG exhibit a permeance up to ten times higher than PSf membranes prepared using different additives and also similar or even higher retentions. Surface segregation of amphiphilic copolymers has long been evidenced to enhance the membranes hydrophilicity and permeability. However, the present work reveals that another permeability-enhancing effect of the amphiphilic copolymers (permeation through water-permeable microdomains) concurs when the dosages of the copolymer are comparable to that of the base membrane-forming materials in addition to the effect of surface segregation. This new role of amphiphilic copolymers has never been reported before and it offers us new possibilities for the development of advanced membranes with the assistance of amphiphilic copolymers.

2. Experimental

2.1. Materials

PSf (P3500 LCD, average molecular weight 22000 Da) supplied by Solvay, was used as the base polymer in the membrane casting solutions. Reagent grade *N*-methyl-2-pyrrolidone (NMP) was used as the solvent to dissolve the polymers without further purification. Reagent grade PEG homopolymer (average molecular weight 400 Da) or PSf-*b*-PEG BCP (the weight ratio of PEG blocks in the copolymer is 49%) were used as the blend components in casting solutions. Deionized water (conductivity: 8.20 $\mu\text{S}/\text{cm}$, Wahaha) was used as the main nonsolvent in the coagulation bath. Bovine serum albumin (BSA) was purchased from Sigma-Aldrich.

2.2. Preparation of PSf/PSf-*b*-PEG and PSf/PEG blend membranes

The casting solutions of 16% in weight were prepared by dissolving PSf and PSf-*b*-PEG in NMP at desired proportions (BCP percentages ranging from none to 70% in the total amount of polymers) under mechanical stirring at 70 °C for 4 h. The casting solutions were kept for at least 48 h at 70 °C in vacuum oven to remove air bubbles. After removal of the air bubbles, the liquid dope was cast onto a glass plate with a casting knife to obtain a casting film of 250 μm thick, then coagulated in deionized water at room temperature. The obtained PSf/PSf-*b*-PEG membrane was thoroughly washed with water to remove the residual NMP. The method of preparing PSf/PEG membranes is the same as the PSf/PSf-*b*-PEG membranes, by replacing PSf-*b*-PEG block polymer with PEG homopolymer.

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