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pH-responsive poly(ether sulfone) composite membranes blended with amphiphilic polystyrene-*block*-poly(acrylic acid) copolymers

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ABSTRACT

pH-responsive poly(ether sulfone) (PES) composite membranes blended with amphiphilic polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) diblock copolymers are fabricated through simple phase inversion in water. The anchor block PS has a lower surface tension than that of PES, which is beneficial to anchor the PS block near the membrane pore surfaces. Modification of membrane matrix surface including membrane surface and pore surface by PAA chains is achieved by surface-segregation of PS-*b*-PAA copolymers, and confirmed by water contact angle measurement on membrane surface and confocal laser scanning microscopy characterization of membrane cross-section. The effects of the blended PS-*b*-PAA copolymers on the microstructures and pH-responsive characteristics of the PES composite membranes are investigated systematically. The hydraulic permeation results show that the pH-responsive characteristics of composite membranes blended with PS-*b*-PAA copolymers are proven to be significant, fast, reversible and durable with pH switching between 3 and 8. FITC-dextran sieving experiments of a PS-*b*-PAA blended composite membrane at ambient pH values of 3 and 8 show 28% and 90% rejection of 70 kDa solute, respectively. At pH=3 ($<\mathrm{p}K_a$), the membrane pores are in "open" state because of the shrunken conformation of the PAA chains on the pore surfaces; in contrast, at pH=8 ($>\mathrm{p}K_a$), the membrane pores are in "closed" state due to the swollen conformation of the PAA chains. The results provide valuable guidance for fabricating stimuli-responsive membranes by blending amphiphilic block copolymers.

1. Introduction

Stimuli-responsive smart membranes that could self-regulate their permeability and separation characteristics responding to environmental stimuli have been drawing considerable attention continuously [1–6]. To date, several types of smart membranes, which can respond to different types of environmental stimuli such as pH [1,7–31], ionic strength [7,32], temperature [33–39], chemical species [40–42], specific metal ions [43–46], electric field [47], light [48], redox potential [49], have been designed and fabricated. Such smart membranes are highly attractive for potential applications in controlled release of chemicals and drugs, biological/chemical separations, tissue engineering, water treatment, sensors and actuators, and so on. As pH is a crucial parameter in many cases and its variation is very common under many conditions, the development of pH-responsive smart membranes is of both scientific and technological interest.

Stimuli-responsive membranes, consisted of porous membrane substrate and surface-tethered functional polymer chains, are mostly fabricated by grafting functional polymer chains onto membrane pore surface. For pH-responsive membranes, the surface-tethered chains are usually weak polyelectrolytes or polypeptides [9,11] that could adjust themselves reversibly between an extended and a compacted conformation according to environmental pH and ionic strength, thus influencing effective pore size of membranes. Manifold methods have been employed to fabricate pH-responsive membranes, and can be classified into three categories based on whether the functional polymer chains are introduced *before*, *during* or *after* the membrane formation.

Introducing functional polymer chains *before* the membrane formation is achieved by grafting pH-responsive functional polymer chains onto hydrophobic membrane materials first, and then utilizing the modified materials alone or blended with pristine

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ones to fabricate pH-responsive membranes. Electron beam or γ-ray radiation [27], O_3 pretreatment [16], UV [28], radical initiator [29] and self-borne ATRP initiating sites of membrane materials [14,23] make it possible to grow the functional polymer chains from membrane materials. Kang et al. [15] and Mayes et al. [14] have reported pioneering works on pH-responsive membranes fabricated with such methods. If the direct modification of membrane materials is easily attainable, it is possible to fabricate pH-responsive membranes on industrial scale with currently existed equipments. However, this kind of method for preparing pH-responsive membranes has not been popularized up to now, because syntheses of copolymeric membrane materials with responsive chains are still not so convenient and controllable yet [50].

In contrast, introducing pH-responsive functional polymer chains onto the membrane substrate *after* the formation of membrane substrate is the majority of methods in previous works. It is realized by post-fabrication modification of porous membranes via “graft-from” or “graft-to” approach to tether pH-responsive polymer chains on membrane surfaces. Through inducing active sites on solid membrane surface first, and then polymerizing functional monomers to yield pH-responsive polymer chains on membrane surface is called the “graft-from” method. Various techniques, including plasma treatment [8,9], UV [7,10,12,19], radical initiator [17] and redox system [22], surface-bond atom transfer radical polymerization (ATRP) initiator [24,25], surface entrapment of radical initiator [18], are accessible to induce the active sites on solid membrane surfaces. By contrast, the “graft-to” method involves covalent binding of the active groups of a pH-responsive polymer chain to attachable sites on membrane pore surface [11,13]. Usually membranes need to be pre-treated to create such attachable sites. The “graft-from” and “graft-to” methods could be applied to modify the most wide range of membrane materials; however, there exist some common problems for the grafting modification methods to be scaled up, such as membrane pore size variation, limited controllability and surface chemistry disparity (except for surface-initiated controlled polymerization such as ATRP), and sophisticated surface pretreatment steps.

Another approach to prepare pH-responsive membranes is introducing pH-responsive functional polymers *during* the membrane formation, which is to blend membrane materials with responsive functional polymers in the form of homopolymers or block/graft copolymers. It is a one-step method and might be easily scaled up if proper responsive functional polymers are available. Such a method has been widely applied in preparation of anti-fouling membranes with hydrophilic surface recently [51–53]. To achieve long-term stability of surface chemistry, it is preferential to utilize amphiphilic block copolymers, with hydrophobic blocks supplying stability and functional hydrophilic blocks delivering surface functionality. Zhu et al. [30] prepared dual pH and thermo-responsive membranes by blending F127 (PEO_{100}-*b*-PPO_{65}-*b*-PEO_{100})-based pentablock copolymers with poly(ether sulfone) (PES). Jiang et al. [31] took advantage of sequential free radical solution polymerization of butyl methacrylate (BMA) and methacrylic acid (MAA) to synthesize a block-like PBMA-*b*-PMAA copolymer, and studied the pH-dependent water permeability of PES membrane blended with PBMA-*b*-PMAA copolymer. However, the structure complexity and consequent sophisticated solution phase behavior of the F127-based pentablock copolymers [54] made it somewhat difficult to relate copolymer structure with membrane morphology and performance, and the PBMA-*b*-PMAA copolymer structure is still not well-defined because the co-existence of some random copolymers. Therefore, to establish a more solid foundation for the platform of fabrication of pH-responsive membranes by blending amphiphilic pH-responsive block copolymers during the membrane formation, it is still necessary and essential to employ a well-defined linear amphiphilic pH-responsive diblock copolymer to fabricate pH-responsive membranes and to investigate the effects of copolymer structure on the membrane morphology and pH-responsive characteristics. With the development in controlled radical polymerization, it is now possible to synthesize amphiphilic block copolymers with well-defined macromolecular structures.

In this work, we report on the fabrication of pH-responsive PES composite membranes by blending amphiphilic diblock polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) copolymers through phase inversion, and the investigation on the effects of copolymer structure on the membrane morphology and pH-responsive characteristics. The fabrication process and pH-responsive gating function of the proposed membranes are schematically illustrated in Fig. 1. The block copolymers are synthesized by a two-step ATRP of styrene and *tert*-butyl acrylate (*t*BuA) to form PS-*b*-P*t*BuA copolymers and subsequent hydrolysis of P*t*BuA blocks. The surface tensions of PES and polystyrene (PS) polymers are derived from liquid contact angle data. Enrichment of PAA blocks on the membrane surface and throughout the cross-sectional channels is verified by water contact angle measurement and fluorescent dye stain characterization. The effects of PS-*b*-PAA copolymer addition, PAA block polymerization degrees and copolymer blend amount on the membrane morphology and pH-responsive characteristics are investigated systematically. The results in this study provide valuable guidance for fabricating pH-responsive membranes by blending amphiphilic block copolymers during the membrane formation.

2. Materials and methods

2.1. Materials

PES (M_w=40,000) is purchased from Changchun Jida New Materials, China. Styrene, toluene, tetrahydrafuran (THF), methanol, acetone, dioxane, concentrated hydrochloric acid (35 wt%), polyethylene oxide 20,000 (PEG 20,000), *N*,*N*-dimethyl acetylamide (DMAc), citric acid dihydrate, disodium phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), CuBr and CuCl, neutral Al_2O_3 are all from Kelong Chemicals, China. *N*,*N*,*N*′,*N*″,*N*″-pentamethyl diethylenetriamine (PMDETA), methyl 2-bromoisobutyrate (2BiB), fluorescein isothiocyanate labelled dextran (FITC-dextran) molecules of molecular weights 10 (FD10S), 40 (FD40S) and 70 kDa (FD70S) are from Sigma. Monomer *tert*-butyl acrylate (*t*BuA) is from Tokyo Chemical Industry. Rhodamine B is from Shanghai Chemical Reagents, China. Tricresyl phosphate is supplied by Sinopharm Chemical Reagents, China. Dialysis bags (MD34, MWCO of 3500 and 8000–14,000) are supplied by Union Carbide, USA. Deionized (DI) water with a resistance of 18.2 MΩ (25 °C) from a Millipore Milli-Q system is used through all the experiments.

2.2. Synthesis of polymer additives

The targeted block copolymers PS-*b*-PAA are synthesized according to a procedure similar to a reported method [55]. Briefly, styrene is solution polymerized in toluene at 90 °C to a conversion of ca. 40% with 2BiB and CuBr/PMDETA as initiator and catalyst, respectively. Then, the bromo-terminated polystyrene is employed as macroinitiator to perform chain extension with *t*BuA. The polymerization is conducted at 80 °C, with CuCl/PMDETA as catalyst and 35 vol% acetone as solvent. Purification of block copolymers PS-*b*-P*t*BuA is accomplished by firstly diluting reaction mixture with THF, then filtering solution through an activated neutral Al_2O_3 packed column, and finally precipitating into a medium of methanol and water (1:1 by volume). Dissolution and precipitation are repeated twice and the