



Composition and properties of porous blend membranes containing tertiary amine based amphiphilic copolymers with different sequence structures



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ABSTRACT

Four tertiary amine based amphiphilic copolymers with similar composition but different sequence structures in terms of diblock (Poly(dimethylamino-2-ethyl methacrylate-*b*-methyl methacrylate) (P(MMA-*b*-DMAEMA))), triblock (P(DMAEMA-*b*-MMA-*b*-DMAEMA)), four-armed diblock (P(MMA-*b*-DMAEMA)₄) and random (P(MMA-*r*-DMAEMA)) were synthesized and used for fabricating functional porous membranes by blending method. The retention ratios and surface enrichment ratios of the copolymers in blend membranes were determined by hydrogen nuclear magnetic resonance (¹H-NMR) and X-ray photoelectron spectroscopy (XPS). The composition of the formed membranes was investigated and the durability was experimentally tested. The hydrophilicity of the membranes was evaluated by water contact angle measurement. The performance of membranes under different conditions including water fluxes at different pH and various ionic strength, the adsorption capabilities for Cr(VI) and negatively charged dye sunset yellow at different pH was studied. The results show that tertiary amine based amphiphilic copolymers with block and multi-armed sequence structures enable the blend membranes with higher copolymer retention ratios, more surface tertiary amine groups contents and better composition stability as well as more sensitive to the variation of pH, ionic strength, higher equilibrium anions, and negatively charged dyes uptakes.

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1. Introduction

Membrane-based separation technology has been widely applied in waste water treatment, food technology, biotechnology, pharmaceutical industries and so on [1,2] due to its efficiency, ease of implementation and cost effectiveness. Much recent researches have been devoted to control the membrane separation performance and to improve the membrane permeability. Membranes with various properties have been developed and fabricated in terms of the selectivity and separation accuracy [3,4], anti-fouling properties [5–8], biocompatibility [9,10] and environment stimuli-responsive [11,12], etc. These membranes have provided and will continue to enable many valuable applications in water treatment, pollutants removal, fine separation, hemodialysis and other fields in the future.

Previous attempts to fabricate functional porous membranes were mainly focused on the construction of functional interfaces

between membrane surfaces or porous walls and separation medium. There are four types of methods for functional surface construction, including surface-coating [13,14], surface-grafting [15–19], copolymer directly formation [20–22], and blending [6,7,23–27]. Surface coating is an efficient and easy-to-operate method that directly covers a functional layer onto the membrane surface by physical adsorption interaction. However, the functional layer constructed by surface coating is commonly unstable and may be washed away during the operation process. In surface grafting, functionalized groups or polymer chains can be grafted to the membrane surface to endow the membrane with various properties with the help of plasma [15], high energy electron beam [16], UV photo irradiation [17], thermal-induced polymerization [18], or surface living/controlled polymerization [19]. Although the membranes formed using these two methods show outstanding performance, the extra modification step and the great variation in the membrane morphology make these methods unsuitable for industry-scale production. Functionalized copolymers can also be directly used to prepare membranes with improved performance. However, the use of relatively high-priced

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materials makes this approach not viable in large scale production. Blending is a single-step approach for modifying porous membranes and is being frequently used to fabricate functionalized membranes with proper additives during the membrane preparation process. This method is efficient, economical and has great industrialization potential. The core of this method is the use of additives such as functionalized polymers [23], functionalized polymer containing particles [6,24] and functionalized amphiphilic copolymers [7,25–27]. However, the elution of additives during the application process seriously influences the stability of membrane composition which further influences the performance. This problem needs to be adequately addressed in future research. To enhance the stability of membrane composition, studies have shown that amphiphilic copolymers with both functionalized segments and the hydrophobic segments are the most competitive additives. Functionalized segments provide the novel properties and hydrophobic segments enhance the retention degree. Amphiphilic copolymers with different sequence structures have been utilized to successfully prepare functionalized membranes, for instance comb-like PVDF-*g*-PMAA [25], multi-block copolymer PDMAEMA-*b*-F127-*b*-PDMAEMA [26], random structure copolymer poly (MMA-*r*-AA-*r*-VP) [27], hyperbranched star copolymer [7]. But functionalized amphiphilic copolymers with proper sequence structures are still being pursued to prepare functionalized membranes with stable membrane composition by blending. In addition, further research is needed on the influence of copolymers sequence structure on the membrane composition.

The choice of hydrophobic and hydrophilic monomers is critical for amphiphilic copolymers. Methyl methacrylate (MMA) is a low-cost hydrophilic monomer which can be easily polymerized to a desirable sequence structure and can be copolymerized with many functional monomers [28,29]. The compatibility between PMMA and typical membrane materials poly(vinylidene fluoride) (PVDF) and poly(vinyl chloride) (PVC) makes MMA a suitable monomer for synthesizing amphiphilic copolymers with desirable sequence structures for PVDF based blend membranes [33–37]. Dimethyl-amino-2-ethyl methacrylate (DMAEMA), a tertiary amine group containing water soluble monomer, is frequently used to synthesize functionalized polymers and functionalized amphiphilic copolymers. Some novel and valuable properties including hydrophilicity [5,19,20,22,26], temperature [19,26], pH [19–21,26], ionic strength [19,22] stimuli-responsive behaviors, drugs adsorption ability [35], anions [36,37] adsorption properties, will be endowed to the pristine matrixes, when using PDMAEMA as modifiers. Furthermore, with some simple chemical modification, the PDMAEMA containing membranes can even exhibit the antibacterial properties after having been quaternized [38] and fouling-resistance after zwitterionization [5]. The above discussion indicates that it is valuable to explore a proper method to prepare tertiary amine containing membranes.

This work aims at studying methods of preparing porous blend membranes with stable composition and performance using tertiary amine based additives. Four tertiary amine based amphiphilic copolymers with different sequence structures, such as diblock, triblock, four-armed diblock and random, were synthesized using DMAEMA as functional monomers and MMA as hydrophilic monomers by atom transfer radical polymerization (ATRP) or by free radical polymerization. Then the synthesized additives were blended with PVDF to form porous membranes by non-solvent induced phase separation (NIPS) process. By measuring the retention ratios and the surface enrichment ratios of the additives, composition of membrane matrix and surface influenced by the copolymers were compared. The composition of the formed membranes was investigated, the durability was experimentally tested, and the stability of the blend membrane composition was evaluated. The hydrophilicity of the membranes was evaluated by water

contact angle measurement. The performance of membranes under different conditions including water fluxes at different pH and various ionic strength, the adsorption capabilities for Cr(VI) and negatively charged dye sunset yellow at different pH was studied. Accordingly it was expected to develop a fundamental understanding of the relation between the sequence structure of tertiary amine based amphiphilic copolymers and the composition, stability, and behavior of the corresponding blend membranes.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) (FR-904, $M_n = 380,000$, Shanghai 3F new materials Co. Ltd., China) was dried at 110 °C for 12 h before use. The tertiary amine based amphiphilic copolymers were diblock copolymer P(MMA₈₆-*b*-DMAEMA₁₀₂) (PMD-1, see [Supplementary material](#) for Syntheses), triblock copolymer P(DMAEMA₁₀₂-*b*-MMA₁₆₆-*b*-DMAEMA₁₀₂) (PMD-2, see [Supplementary material](#) for Syntheses), four-armed copolymer P(MMA₈₈-*b*-DMAEMA₁₀₆)₄ (PMD-3, see [Supplementary material](#) for Syntheses) and random copolymer P(MMA₇₇-*r*-DMAEMA₁₀₂) (PMD-4, see [Supplementary material](#) for Syntheses). Other chemicals such as N,N-Dimethylacetamide (DMAc), potassium dichromate (K₂Cr₂O₇) and sunset yellow were directly used without further purification.

2.2. Membrane fabrication

The casting solutions were prepared by dissolving 16 wt% PVDF and 2 wt% diblock copolymer (M1) or triblock copolymer (M2) or four-armed diblock copolymer (M3) or random copolymer (M4) in 82 wt% DMAc at 60 °C for 24 h, respectively. In contrast, the casting solution of pure PVDF membrane (M0) was prepared by dissolving 16 wt% PVDF in 84 wt% DMAc under the same conditions. After releasing the bubbles under reduced pressure (–50 kPa) for 30 min, the homogeneous casting solution was spread into liquid film on a glass plate with a steel knife. Then, the liquid film on the glass plate was immediately immersed into a coagulation bath of deionized water at 30 °C. The formed membranes were peeled off, washed with deionized water to remove residual solvent, and dried for 24 h at room temperature before characterization.

2.3. Membranes characterization

The surface and cross-section (fractured in liquid nitrogen) morphologies of prepared membranes were inspected by scanning electron microscopy (SEM, S-4800 Hitachi, Japan) after being coated with platinum. To study the composition in membrane matrix, the prepared blend membranes were dissolved in deuterated dimethyl sulfoxide (DMSO-*d*₆) and measured by ¹H-NMR (NMR300, Varian, USA). X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA system, PHI Co., USA) was used to measure the composition in surface layer of the blend membranes. Al K α radiation (1486.6 eV) was used as X-ray source and run at a power of 250 W (14.0 kV, 93.9 eV) with an electron takeoff angle of 30° relative to the sample plane. The water contact angle on the membrane surface was measured using an optical instrument (OCA20, Dataphysics, Germany) equipped with video capture at 25 °C for predicting hydrophilicity. The thermal behaviors of membranes were studied by a differential scanning calorimeter (DSC, Q200, TA, USA). Approximately 5–9 mg of samples was sealed in aluminum pans and thermograms were recorded from –20 °C to 220 °C at a heating rate of 10 K/min under a constant flow of

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