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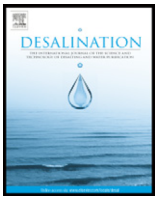

Preparation and characterization of PVDF-P(PEGMA-r-MMA) ultrafiltration blend membranes via simplified blend method

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HIGHLIGHTS

- Simplified blend method was beneficial to micro-stricture adjustment of PVDF casting solution.
- PVDF membranes possessed narrow distribution pore size and molecular weight cut off (MWCO).
- Ethanol coagulant resulted in obvious tunable morphologies and hydrophilicity improvement.

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ABSTRACT

P(PEGMA-r-MMA) amphiphilic copolymer with Mn of 66,500 g/mol and Mw of 34,200 g/mol was successfully synthesized via free radical polymerization. And polyvinylidene fluoride (PVDF)-P(PEGMA-r-MMA) blend membranes were fabricated from water and ethanol coagulants via simplified blend method by directly blending PVDF and P(PEGMA-r-MMA) amphiphilic copolymer solution (including the reaction mixture) to form casting solution. The formation of the supramolecular aggregates in PVDF solution containing the copolymer were confirmed by dynamic light scattering and scanning electron microscopy. This contributed to the micro-structure adjustment of PVDF solution and resulted in its decreasing surface tension, accelerating precipitation rate and increasing viscosity with trivial strain thinning behavior. Furthermore, the effects of the variations in dopant contents and coagulant compositions on the performances of those blend membranes were investigated. All PVDF-P(PEGMA-r-MMA) blend membranes possessed narrow distribution mean effective pore size (μ), molecular weight cut off (MWCO), improved recovery water flux after filtration experiments of bovine serum albumin and tuned configurations. Compared with the instantaneous demixing process in water coagulant, the delayed demixing process in ethanol favored the pore-forming and surface segregated of the polar head group of the copolymer, which induced the increasing μ, MWCO, tunable morphologies and hydrophilicity improvement.

1. Introduction

Porous polymeric membranes have widespread applications in water and wastewater purification, desalination and gas separation. PVDF is advantageous over other polymeric materials due to its high mechanical strength and excellent chemical resistance, and thus these properties make it suitable for purification and separation. However, the functions of PVDF membranes are greatly influenced by their physical morphologies and chemical compositions. The optimized-structure of PVDF in terms of the membrane surface properties, morphologies and mechanical properties are anticipated for various applications in areas of wastewater treatment. Special emphasis is given on the effects of various parameters involved in the preparation of PVDF membranes with hydrophilicity modification from phase inversion process [1]. Precise control over the porous morphology of the membranes to meet the specific requirements via non-solvent induced phase separation (NIPS) process can be achieved by tuning various experimental parameters, including the ratio of polymer dope formulation, the type of solvent and additive, the amount of additive, preparation temperature and composition of coagulant. Synthetic pore-forming amphiphiles agents with segregated hydrophilic and hydrophobic moieties in the structure have attracted many researchers' attention in recent years [2–5]. Even the simplest class of the amphiphiles, the head or tail surfactants, can form a wide variety of self-assembled structures, depending on the relative volumes of the hydrophilic and hydrophobic components [6]. Usually, the amphiphilic polymers have been used as the models to study the microphase separation in the bulk and self-assembling behavior in the solution because of the nonionic and highly crystalline

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nature of poly(ethylene glycol) (PEO) [7]. P(PEGMA-r-MMA) amphiphilic copolymers prepared via free radical polymerization are among them with the common head or tail surfactants. It is speculated that the self-assembled structures of the P(PEGMA-r-MMA) amphiphilic copolymers in polymer solution might play an important role in the micro-structure modulation of PVDF membranes.

Besides, a good solvent is essential in formulating a uniform polymer solution, and in obtaining the membranes with tunable morphologies and performances. It has been reported that N,N-dimethylacetamide (DMAc) and triethyl phosphate (TEP) are solvents for PVDF. PVDF polymer dissolved fairly easily in DMAc, but it did not easily dissolve in TEP [8]. As a strong solvent, when DMAc is used as solvent, PVDF membrane always exhibits finger-like macrovoids structure. Nevertheless, the membranes cast with TEP as solvent exhibit symmetry sponge structure and excellent mechanical property [9]. TEP-DMAc has been adopted as co-solvent to prepare PVDF membranes with anticipation properties [10]. In this study, TEP-DMAc (70:30, mass ratio) is used as co-solvent to obtain targeting PVDF membrane with sponge-like cross sectional structure and increase pore size with narrow distribution in its top-surface. Additionally, as for coagulants, water is well-known the harsh non-solvent, which has high diffusive rate with many solvents. Methanol, ethanol and 1-octanol are the common soft non-solvents [11,12]. As soft non-solvent, ethanol is not only used as the coagulant to slow down the precipitation rate, but also to post-treat the pristine membranes [13]. Based on the synergetic consideration of the mass transfer rate between the coagulants and the casting solutions, water and ethanol are chosen as coagulants to provide the information on the modulation route of P(PEGMA-r-MMA) amphiphilic copolymer during various demixing processes.

In this study, we aim to obtain tuned behavior of the supramolecular aggregates via simplified blend method by directly blending PVDF and the P(PEGMA-r-MMA) amphiphilic copolymer solution (including the reaction mixture) to form the PVDF casting solution [14]. Thus, the simplified blend method is expected to provide the morphology modulation of the PVDF membranes by tuning the micro-structure of the polymer solution with the presence of the P(PEGMA-r-MMA) amphiphilic copolymer. The reasons that the simplified blend method prevails in comparison to those regular blend methods are as follows. On one hand, the simplified blend method is environment-friendly; it is utilized to reduce the overall costs associated with the membrane preparation process, avoiding further surface modifications of the PVDF membranes. On the other hand, the excess or unreacted PEGMA and MMA monomers can act as pore-forming agents in the membranes and are expected to be washed out during the NIPS process [15]. Furthermore, DLS and SEM are utilized to investigate the conformation adjustment of PVDF in the solution containing P(PEGMA-r-MMA) amphiphilic copolymer. And the influences of the variations dopant contents and coagulant compositions on the performances of the PVDF-P(PEGMA-r-MMA) blend membranes were investigated.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF, Solef® 6010) was purchased from Solvay Advanced Polymers, L.L.C (Alpharetta GA, USA). DMAc, MMA, Al_2O_3 (basic), ethanol, triethyl phosphate (TEP), azobisisobutyronitrile (AIBN) were purchased from Shanghai Sinopharm Chemical Reagent Co. LTD (China). Polyethylene glycol monomethyl ether methacrylate (PEGMA, Mn = 1200, industrial grade) was a mahogany liquid and was supplied by Taijie Chemical Co. LTD (China, Shanghai). Bovine serum albumin (BSA) (MW 67 K) and Dextran (MW 40 K, 70 K, MW 100 K, MW 500 K and MW 2000 K) were purchased from Lianguan Biochemical Reagent Company of Shanghai and Sigma-Aldrich Co., respectively. Deionized water was prepared by our own lab. PEGMA and MMA were purified by basic Al_2O_3, while AIBN was recrystallized in ethanol. All other chemicals used in the experiments were analytical grade and were used without further purification.

2.2. Synthesis of P(PEGMA-r-MMA) amphiphilic copolymer

The typical synthesis route of P(PEGMA-r-MMA) amphiphilic copolymer was as follows. PEGMA (120.0 g, 0.1 mol), MMA (6.6 g, 0.06 mol) and TEP (70.4 g) mixture was purified by 4.0 wt.% basic Al_2O_3, and then the mixture was charged into a conical flask with plug and stored in a dark place for further use. The nitrogen gas was bubbled through the reaction solution, and the reaction vessel was sealed with a septum. A certain amount of recrystallized AIBN ([AIBN]/[MMA + PEGMA + TEP] = 1/100, mass ratio) was added to the corresponding solution and then the reaction solution was heated to 70 °C; the polymerization was carried out at 70 °C with stirring for 2 h. The synthesis route of P(PEGMA-r-MMA) was shown in Fig. 1. Then, some amount of reaction solution mixtures were cooled to ambient temperature and dialyzed by a bag filter (RC-44-7K, Greenbird Science & Technology Development Co., Ltd, Shanghai) of 7000 molecular weight cut off (MWCO). After being dialyzed in the stirring deionized water for two days (water was changed every 3 h), the copolymer was recovered by freeze drying (FD-1C-50, Beijing Boyiyang Instrument, CO. LTD).

2.3. Characterization of P(PEGMA-r-MMA) amphiphilic copolymer

After purification, the construction of P(PEGMA-r-MMA) amphiphilic copolymer was characterized by ^1H NMR, gel permeation chromatograph (GPC) and Fourier Transform Infrared Spectrometer (FT-IR). ^1H NMR spectrum was recorded on a Bruker BioSpin GmbH (Germany) operated at 400 MHz, using D_6-DMSO and tetramethylsilane (TMS) as solvents and internal standard, respectively. Molecular weight and molecular weight distribution of styrene/purification P(PEGMA-r-MMA) amphiphilic copolymer were investigated by a GPC system of a Waters 1525 (Waters CO., USA). Tetrahydrofuran (THF) was used as eluent with a flow rater of 1.0 mL/min at 35 °C, and the concentration of sample was 0.5 wt.%. Fourier Transform Infrared spectra of the copolymer samples were measured on a Bruker Vector 22 FT-IR Spectrometer (Switzerland).

2.4. Preparation of PVDF-P(PEGMA-r-MMA) blend membranes

Various concentrations of P(PEGMA-r-MMA) solution (including the reaction mixture) were directly blended with PVDF to form casting solution in co-solvent. After PVDF was completely dissolved at 80 °C, and standing time of the casting solution was at least 12 h

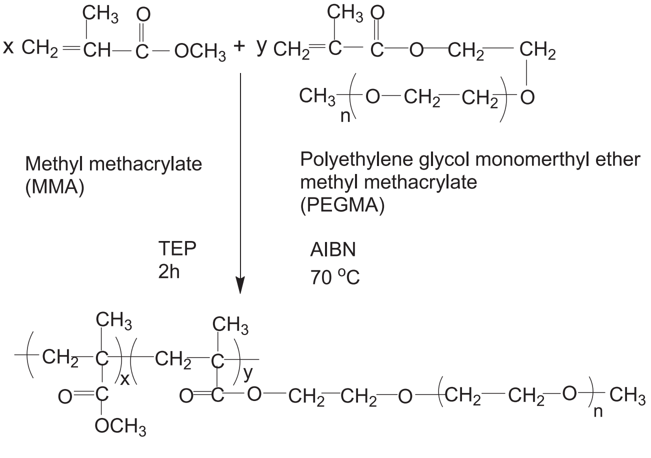

Fig. 1. The synthesis route of P(PEGMA-r-MMA) amphiphilic copolymer.