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Fabrication and characterization of PVDF hollow fiber membranes employing in-situ self-assembly modulation concept

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ABSTRACT

We develop a novel polyvinylidene fluoride (PVDF) hollow fiber membrane utilizing the concept of in-situ self-assembly modulation, which is in terms of in-situ synthesis of amphiphilic copolymers and in-situ solubilization of polyvinylpyrrolidone (PVP). Utilizing the polytetrahydrofuran dimethacrylate ester (PTMGDA) and polyethylene glycol monomethyl ether methyl methacrylate (PEGMA) as reaction monomers, amphiphilic copolymers are in-situ synthesized, denoted as "P(PTMGDA-r-PEGMA)". Results show that P(PTMGDA-r-PEGMA) and PVP have the synergistic effects on configuration and separation performance of PVDF membrane. P(PTMGDA-r-PEGMA) with high ratio in hydrocarbon chain (75.2%) and PVP not only effectively tunes micro-structure of the dope solutions but also results in the enhancement of the resultant membranes' break strength and their stable permeability. Besides, the supramolecular aggregates of PVDF-P(PTMGDA-r-PEGMA)–PVP (size: 76–157 nm) work as "template" dependence of the macrovoids, which appear in the fibers' sponge-like cross-section structure, hence leading to the narrowing pore size distribution. Furthermore, the macrovoids' size enlarges with the increase of content of P(PTMGDA-r-PEGMA) and PVP. It is also found that the permeation flux is controlled by the diffusion of PVP from the interior dope solution and pore-forming of P(PTMGDA-r-PEGMA) during demixing process, which is consistent with the in-situ self-assembly modulation concept. Finally, the newly developed PVDF hollow fiber membranes demonstrate remarkable long-term stable permeability.

1. Introduction

Membrane technology has been emerging as a competitive candidate among the technologies for reclamation and reuse of water. Membrane has been utilized to capture water from the nontraditional waste-water sources in terms of hydrocarbon processing, metallurgical, pharmaceutical, food industries and so on, to restore the waste-water to potable or irrigation quality water [1]. PVDF has been paid great attentions as one of the membrane materials with outstanding properties such as strong mechanical properties, good thermal stability, good chemical resistance and high hydrophobicity. By now, PVDF membranes have been extensively applied in many applications, such as in the separation process of the ultrafiltration and microfiltration, and membrane contactor and membrane distillation [2]. However, there is still a challenge for the PVDF membranes to treat aqueous solution containing natural organic matters due to their low surface energy. Faced with this challenge, the performance improvement of PVDF membranes has been attached great importance on good permeability and improved fouling resistance. Because aggregates with different structures and morphologies in the dope solution have great impact on these properties [3], many methods by adjusting molecular structure, copolymer concentration and solution temperature, and adding additives are utilized to form different aggregation morphologies, such as spherical, rodlike, even wormlike and inverted micelles, vesicles and flexible bilayers [4].

Self-assembly of amphiphilic copolymers in solution is well-known in colloids and materials research [5]. Development of novel amphiphilic copolymers as additives is of significance in both theories and applications [2,6] to improve membrane properties. Amphiphilic copolymers simultaneously have both hydrophilic head groups and hydrophobic tails. In the amphiphilic copolymers, hydrophilic groups have a close affinity to a polar (aqueous) medium,

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Abbreviations: PVDF, polyvinylidene fluoride; PVP, polyvinyl pyrrolidone; PTMGDA, polytetrahydrofuran dimethacrylate ester; PEGMA, polyethylene glycol monomethyl ether methyl methacrylate; MMA, methyl methacrylate; PEOM, polyoxyethylene methacrylate; RAFT, fragmentation chain transfer polymerization; ATRP, atom transfer radical polymerization; TEP, triethyl phosphate; DMAc N, N-dimethylacetamide; AIBN 2, 2-azobisisobutyronitrile; BSA, bovine serum albumin; MWCO, molecular weight cut-off; FRR, flux recovery ratio

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whereas hydrophobic tails have a close affinity to the selective non-polar solvent [7]. This structural specificity can be beneficial for good aggregation morphologies.

However, to our best knowledge, few satisfied approaches using amphiphilic copolymer are reported for membrane fabrication. As an alternative approach, amphiphilic copolymers' self-assembly via blending is to incorporate directed water channels in the membranes and endow PVDF membrane hydrophilic modification with desirable morphology and mechanical integrity [8]. Another irreplaceable advantage of amphiphilic copolymers utilized as blending membrane additive is its integration of self-assembly modification and phase inversion fabrication of the PVDF membrane [2]. In 1999, Mayes et al. [9] firstly developed a P(MMA-r-POEM) amphiphilic comb-like copolymer as a blending additive. Since then, a great amount of researchers have been focusing on copolymers synthesis and applications in the area of hydrophilic and anti-fouling modifications for the PVDF membrane [10]. Amphiphilic copolymers could be synthesized via thermal graft copolymerization [11,12], general radical polymerization [13–16], reversible addition-fragmentation chain transfer polymerization (RAFT) [17–19], and atom transfer radical polymerization (ATRP) and so on [20–24]. Generally, the amphiphilic copolymer after purification is directly blended with PVDF to obtain a homogeneous solution ready to cast or spin [25]. In order to reduce operational recipe and hence overall costs involved in the general blending modification process, a simplified blending method was proposed [26], in which the P(PEGMA-r-MMA) amphiphilic copolymer solution (including the reaction mixture) and PVDF were directly blended to form the PVDF casting solution. However, results showed that the simplified blending method failed to improve the micellization of P(PEGMA-r-MMA), and limited the function of the amphiphilic copolymer with respect to pore forming and morphology modulation [27].

In-situ free radical polymerization has been utilized to improve the micellization of P(PEGMA-r-MMA) with a simple operational recipe and low economical cost in our previous study [28]. PVDF flat sheet membranes with hydrophilicity, superior mechanical behaviors and enhanced antifouling properties were successfully fabricated from PVDF–PEGMA–MMA–TEP–DMAc system with improved micellization of P(PEGMA-r-MMA) [28]. PVDF hollow fiber membranes have some advantages because of the larger module area/volume ratio [29], which determines the membrane wall thickness resistance to pressure. Therefore, the PVDF hollow fiber membranes utilizing the in-situ method are expected to fabricate membranes with good properties. However, our previous method applied for PVDF membranes cannot directly be utilized to fabricate PVDF hollow fiber membranes from PVDF–PEGMA–MMA–TEP–DMAc system after in-situ polymerization, because of the casting solution's low viscosity and the delayed demixing process in water coagulant. Therefore, in-depth understanding of the design and optimizing spinning conditions in hollow fiber membrane formation is required to achieve good PVDF hollow fiber membranes [30]. Considering the solubilization H_2O of Tween 80 reverse micelle in N,N-dimethylacetamide (DMAc) system [31], PVP are tried to be added into the PVDF–PEGMA–MMA–TEP–DMAc system. Hence, first attempt is carried out for in-situ free radical polymerization by adding 2, 2-azobisisobutyronitrile (AIBN) as the initiator. The improvements of thermodynamics stability and membrane-forming behavior are found for the resultant solution. The phenomenon can be explained by in-situ self-assembly modulation concept that the micro-structure adjustment of the dope solutions is caused by P(PEGMA-r-MMA) and PVP after in-situ polymerization. The diffusion route of PVP during demixing process forms the pore channel, which increases the porous stability and favors the surface segregation of the polar head groups of P(PEGMA-r-MMA) [5]. PVDF hollow fiber membranes are successfully fabricated from PVDF–PEGMA–MMA–TEP–DMAc system after in-situ polymerization. However, they are easy to be broken up when they were maintained at 0.1 MPa in the cell for half an hour. The poor quality of the resultant fibers is due to the high ratio of hydrophilic chain in P(PEGMA-r-MMA). Therefore, PTMGDA with longer hydrocarbon chain instead of MMA is used as the reaction monomer, and good PVDF hollow fiber membranes are fabricated from PVDF–PTMGDA–PEGMA–PVP–TEP–DMAc system via in-situ self-assembly modulation.

The primary objective of this paper is to utilize the concept of in-situ self-assembly modulation to further investigate the feasibility of fabricating PVDF hollow fiber membranes. The second objective is to analyze the synergistic effect of P(PTMGDA-r-PEGMA) and PVP on the tune of configuration and performance of modified PVDF hollow fiber membranes, which has not been emphasized previously yet. The correlation among dope solution micro-structure, membrane configuration and filtration property with in-depth science is also discussed.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF, Solef® 6010) was supplied by Solvay Advanced Polymers, L.L.C (Alpharetta GA, USA). Triethyl phosphate (TEP), N,N-dimethylacetamide (DMAc), Al_2O_3 (basic), glycerol, triethyl phosphate (TEP), polyethylene glycol (PEG, MW 1 kg/mol, MW 2 kg/mol, MW 6 kg/mol, MW 10 kg/mol and MW 20 kg/mol) and 2,2-azobisisobutyronitrile (AIBN) were purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd. (China). Bovine serum albumin (BSA) (MW 67 kg/mol) and Dextran (MW 40 kg/mol and MW 70 kg/mol) were supplied by Lianguan Biochemical Reagent Company of Shanghai and Sigma-Aldrich Co., respectively. Polytetrahydrofuran dimethacrylate ester (PTMGDA, MW 1.1 kg/mol) was synthesized in our lab and its detailed structure and chemical composition are provided in Figs. S1–S3 Supplementary data. Polyethylene glycol monomethyl ether methyl methacrylate (PEGMA, MW 1 kg/mol) was supplied by Taijie Chem. Co. Ltd. (China, Shanghai). Polyvinylpyrrolidone (PVP, MW 90 kg/mol) was supplied by Shanghai qifuqing Material Technology Ltd. (China). De-ionized water was prepared in our lab. The other materials used in the experiments were reported in previous research [28].

2.2. In-situ synthesis of P(PTMGDA-r-PEGMA) amphiphilic copolymer

The in-situ synthesis route of P(PTMGDA-r-PEGMA) amphiphilic copolymer is shown in Fig. 1. Firstly, purified by 4.0 wt% Al_2O_3 (basic), the mixture dopant of PTMGDA (6.6 g) and PEGMA (120.0 g) in TEP (70.6 g) is charged into a conical flask with plug and stored in dark environment for future usage. Secondly, charge 12.0 g of the previously prepared dopant and 70.0 g of TEP–DMAc co-solvent (70:30, mass ratio) into a three-necked flask to form the PTMGDA–PEGMA–TEP–DMAc system. Thirdly, after heating at 70 °C in the three-necked flask, 0.12 g of AIBN recrystallized from pure ethanol is introduced into the system with a mass ratio of $[AIBN]/[MMA+PEGMA+TEP]=1/100$. Fourthly, the above reactants' system is continuously stirred for 10 h at 70 °C to make the in-situ free radical polymerization take place. After that, the reaction system is cooled to the ambient temperature, and the amphiphilic copolymer is purified with a bag filter with molecular weight cut off (MWCO) of 14,000 (RC-44-7K, Green-bird Science & Technology Development Co., Ltd., Shanghai). Finally, after dialyzed in de-ionized water changed once every 3 h for two days, the amphiphilic copolymer of P(PTMGDA-r-PEGMA) is recovered by a freeze-drying equipment (FD-1C-50, Beijing Boyiyang Instrument, CO. Ltd.).