



Fabrication of a novel PS4VP/PVDF dual-layer hollow fiber ultrafiltration membrane



Yuanyuan Liu^a, Tianyin Liu^a, Yicheng Su^a, Haoge Yuan^a, Teruaki Hayakawa^b,
Xiaolin Wang^{a,*}

^a Beijing Key Laboratory of Membrane Materials and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

^b Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan

ARTICLE INFO

Article history:

Received 4 November 2015

Received in revised form

24 January 2016

Accepted 25 January 2016

Available online 27 January 2016

Keywords:

Dual-layer membrane

Block copolymer

Self-assembly

Ultrafiltration

Hollow fiber

ABSTRACT

A dual-layer hollow fiber membrane with highly ordered isoporous surface and excellent mechanical strength was fabricated via block copolymer self-assembly and non-solvent induced phase separation. The isoporous outer layer formed by the self-assembly of poly(styrene-*b*-4-vinylpyridine) (PS4VP) was based on a poly(vinylidene fluoride) (PVDF) microfiltration membrane as the robust support layer. The prepared membranes showed high tensile strength between 6.21 and 6.95 MPa. The good adhesion between the layers was ascribed to the infiltration of PS4VP into the porous PVDF support, which in turn increased transport resistance as well. Therefore, intermediate-treatment agents were introduced to reduce the infiltration depth of PS4VP, and the resultant membranes showed improved water permeability and remained interfacial adhesion. The highest water flux of the membranes reached 90.8 L/m² h bar and the molecular weight cut-off was 74 kDa. Such a novel PS4VP/PVDF dual-layer hollow fiber ultrafiltration membrane is a promising candidate for highly selective separation.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Ultrafiltration is widely used for size-based separations in diverse applications, especially in biotechnology processes such as protein concentration, buffer exchange, and enzyme extraction [1,2]. Traditional membrane applications are limited in separation processes with high throughput but low-resolution requirements [3]. One of the most important reasons stems from the relatively low separation capacity of ultrafiltration membranes. The membrane performance still needs to be drastically improved in order to meet the requirements of highly selective separations, for example, the faithful removal of undesired impurities like virus or the efficient separation of biomolecules with similar molecular sizes. The formation of a selective surface layer is critical for the highly selective separation. Moreover, an integral membrane structure with excellent mechanical property is also essential, so that the membrane can sustain long-term operation without fiber failure or significant deterioration.

Poly(vinylidene fluoride) (PVDF) is a well-known semi-crystalline polymer with outstanding mechanical property, high chemical resistance and excellent thermal stability [4]. The PVDF hollow fiber membranes with bi-continuous porous structures

prepared from thermally induced phase separation (TIPS) method have both high mechanical strength and water permeability. The hollow fiber geometry is favorable for modules due to the advantages of high surface-to-volume ratios and ease of module fabrication [5]. However, the pore size on the membrane surface can hardly be controlled under 0.1 μm because of the formation of surface defects. The interpenetrated pore structure of PVDF hollow fiber membrane results in an ideal support for novel dual-layer membrane. Introducing a functional selective layer on the robust PVDF membrane will be an effective approach to obtain a dual-layer membrane with both excellent mechanical property and high selective separation.

Dual-layer hollow fiber membranes have received great research interest because of their potential to merge the properties of both materials which constitute the surface and support layers respectively [6,7]. Functionalized polymers, including zwitterionic polymers and poly(ether sulfones) have been introduced on the PVDF support aiming at enhancing the separation capacity [8,9]. Resultant membranes showed high permeability and tunable molecular weight cut-offs (MWCO) of 33–292 kDa. However, the formation mechanism of the selective layer fell into the traditional scopes, thus the amorphous stacking of polymer chains in the surface layer failed to achieve in a dramatic increase in selectivity.

In this respect, the control of surface pore morphology is crucial to obtain highly selective membranes since ultrafiltration process is mainly based on the sieving mechanism. Recent emphasis has

* Corresponding author.

E-mail address: xl-wang@tsinghua.edu.cn (X. Wang).

been driven on the development of new membranes with well-defined pore architectures [10]. The generation of isoporous membranes from block copolymers (BCPs) is promising owing to the versatility of BCP in self-assembling into ordered structures with periodic and uniform nano-domains [11,12]. By converting the cylinders of the minor blocks into pores, the BCP precursors are amenable to the preparation of membranes hosting highly ordered cylindrical pores with nearly identical pore diameter aligned perpendicularly to the membrane surface [13,14]. Such isoporous membranes promise both sharp selectivity and high permeability, outperforming the conventional membranes with the tortuous porosity and a wide pore size distribution [15].

Selective etching [16–19] and selective swelling [20–23] are two well-known strategies explored to implement isoporous membranes from BCP precursors. Nevertheless, the as-prepared selective layer is not suitable to be applied in the hollow fiber configuration. In recent years, a method combining the BCP self-assembly and non-solvent induced phase separation (NIPS), termed as SNIPS, stands out as a one-step fascinating process for preparing isoporous ultrafiltration membranes [14,24,25]. This simple procedure yields integral asymmetric membranes with an ordered porous top layer above a thick, sponge-like, and macroporous bottom layer. The pores are formed spontaneously during phase inversion. Not any mass loss or any extra post-treatment procedures are necessary, so that it has great upscaling potential. Numerous materials, including poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP, denoted as PS4VP) [26–29], poly(styrene-*b*-2-vinylpyridine) [30,31], poly(styrene-*b*-ethylene oxide) [32,33], and poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) [34–36] have been successfully fabricated into isoporous membranes via SNIPS. Among them, PS4VP is the first reported [29] and most frequently used BCP, due to the strong repulsion between the PS and P4VP chains which endows PS4VP with high tendency of self-assembly [33]. Inspiring work has been carried out to get a deeper understanding of the pore formation mechanism [37–41], focusing on the effective control of well-ordered surface pores with diameters tunable between 20 and 70 nm [42,43]. In addition, reported studies have exhibited good examples of PS4VP hollow fiber membranes with isoporous surfaces [44] and even catalytic activity [26]. However, one of the major challenges in practical applications lies in the mechanical integrity, as the macroporous bottom layer composed of PS4VP beneath the isoporous selective layer is brittle. The handling of membranes usually calls for great care because the PS4VP membranes are easy to break even under very small external forces. Generally the elongation at break of the membrane during the tensile experiment is less than 10%, implying the great limitation of the membranes in practical applications. Moreover, the sole composition of BCP in resultant membranes results in the large amount of consumption of expensive BCP materials. All these reasons confirm that PS4VP is more suitable to constitute the selective layer in a dual-layer hollow fiber ultrafiltration membrane.

In our previous study, the effort has been carried out to explore the feasibility to generate highly ordered structures from BCPs [12], and we have demonstrated the facile morphology control of the single-layer isoporous membranes in flat sheet configuration [45]. Herein, we aimed at further pushing forward this series of work from the more practical aspect. A novel dual-layer hollow fiber ultrafiltration membrane was fabricated by the construction of a PS4VP outside surface layer on a robust and porous PVDF support membrane via a dip-coating and SNIPS process (Fig. 1). The PVDF support provides enhanced mechanical strength and lowers the cost, and the PS4VP layer promises high selectivity, attributed to the unique self-assembled structure. The interpenetration of the dope solution near the interface was controlled by prewetting the PVDF support with different intermediate-

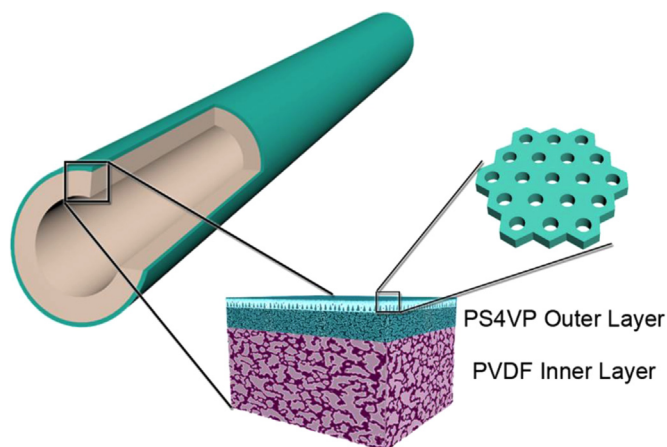


Fig. 1. Schematic diagram of the structure of the dual-layer hollow fiber membrane with PS4VP outer layer and PVDF inner layer.

treatment agents, the effects of which on the membrane structures and water fluxes were investigated. We envisioned that these isoporous membranes will possess attributes useful for various ultrafiltration applications, especially in the evolution of next generation biotechnology processes.

2. Experimental

2.1. Materials

PS4VP powder (number P10900-S4VP, $M_n=188\ 000$ - b -64 000, $M_w/M_n=1.16$) was purchased from Polymer Source, Inc., Canada. Dimethyl formamide (DMF), 1,4-dioxane (DOX), acetone (ACE) and dimethyl sulfoxide (DMSO) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd., China. Poly(ethylene oxide) (PEO) with different molecular weights (2, 6, 20, 100, 200, 300, and 600 kDa) were obtained from Sigma-Aldrich. PVDF hollow fiber micro-filtration membranes with an average pore diameter of outside surface *ca.* 0.15 μm were provided by Asahi Kasei Chemicals Corp., Japan. The porous PVDF hollow fibers had an external diameter of 1.2 mm and an internal diameter of 0.6 mm.

2.2. Fabrication of the dual-layer hollow fiber membranes

Ternary solvent mixture of DMF, DOX and ACE with a weight ratio of 12:21:8 was used for preparation of dope solutions. Certain amount of PS4VP was added into the solvent mixture, and the solution was stirred for 24 h at room temperature until it was homogenous. The dope solution was then stored for another 24 h to remove the air bubbles before use. Before the contact with the PS4VP dope solution, the PVDF hollow fiber membrane was immersed in different intermediate-treatment agents for 5 s in order to control the interpenetration of the dope solution into the porous support layer. The conditions for different samples were shown in Table 1. The membranes prepared at PS4VP concentrations of 16, 17 and 18 wt% without intermediate-treatment agents were named as DL-16, DL-17 and DL-18, respectively. The letters following the sample names represent different intermediate-treatment agents (A for DMF:DOX:ACE=12:21:8 wt%, B for DOX, and C for DOX:ACE=21:8 wt% respectively). Excess drops on the outside surface of PVDF fibers were removed by filter paper after the application of intermediate-treatment agent. Both ends of PVDF fibers were sealed with nails to avoid penetration of the dope solutions into the internal membrane surface.

The dual-layer PS4VP/PVDF hollow fiber membranes were then

Download English Version:

<https://daneshyari.com/en/article/632475>

Download Persian Version:

<https://daneshyari.com/article/632475>

[Daneshyari.com](https://daneshyari.com)