

## Regular Article

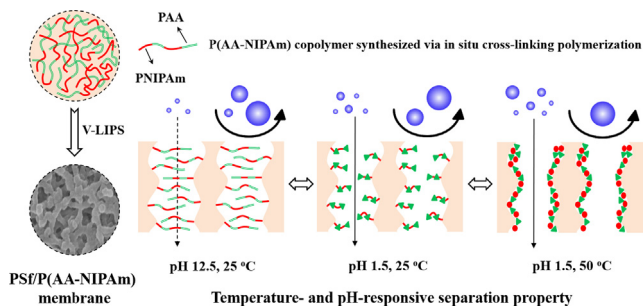
## Dual stimuli-responsive polysulfone membranes with interconnected networks by a vapor-liquid induced phase separation strategy



Li-Jing Zhu\*, Hai-Ming Song, Gang Wang, Zhi-Xiang Zeng\*, Qun-Ji Xue

Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 9 May 2018

Revised 23 July 2018

Accepted 23 July 2018

Available online 24 July 2018

## Keywords:

Polysulfone membranes

Gating membranes

Dual thermo- and pH-response

In situ cross-linking polymerization

Phase separation

## ABSTRACT

Dual pH- and thermo-responsive polysulfone (PSf) membranes with three-dimensionally interconnected networks are fabricated by introducing poly(acrylic acid-co-N-isopropylacrylamide) (P(AA-NIPAm)) into the membrane surfaces and pore walls during membrane formation via a vapor-liquid induced phase separation (V-LIPS) process. After introducing the copolymers of P(AA-NIPAm), the fabricated membranes exhibit impressive open network pores on the surfaces, meanwhile their cross-sectional structure turns from classical asymmetric finger-like structure into bi-continuous nanopores throughout the whole thickness of membrane, due to high solution viscosity and low mass transfer rate of VIPS process. Furthermore, pure water permeation tests show that the pure water permeation ( $L_p$ ) and the molecular weight cutoff (MWCO) of the fabricated PSf/P(AA-NIPAm) membranes increases sharply as the solution pH decreases from 12.5 to 1.5 and the feed temperature increases from 25 to 50 °C, attributing to the increasing pore size. With the decreasing mass ratio of AA to NIPAm, the pH-responsive coefficient decreases, while the temperature-responsive coefficient increases. In particular, for the fabricated membrane with the mass ratio of AA to NIPAm of 3 to 2,  $L_p$  changes from  $\sim 16.0$  to  $\sim 821.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and MWCO increases from  $\sim 223.1$  to  $\sim 1493.2 \text{ kDa}$ , as the filtration experiments are operated with feed pH and temperature of 12.5/25 °C and 1.5/50 °C respectively. The results proposed in this study provide a novel mode for design and development dual responsive porous membranes in situ, which will enable good separation of various materials and expand the scope of membrane applications.

© 2018 Elsevier Inc. All rights reserved.

## 1. Introduction

Membrane techniques have been widely used in myriad fields such as water treatment, desalination, hemodialysis and food

\* Corresponding authors.

E-mail addresses: [zhulijing@nimte.ac.cn](mailto:zhulijing@nimte.ac.cn) (L.-J. Zhu), [zengzhx@nimte.ac.cn](mailto:zengzhx@nimte.ac.cn) (Z.-X. Zeng).

industry, because they are lower cost and easier to operate in large scale than other methods [1–3]. Generally, each membrane possesses certain pore size and surface properties, the permeability and the selectivity are often unalterable for traditional porous membranes due to the lack of changeable physical/chemical structures. As a result, a traditional porous membrane can only separate the solute with a single diameter. To expand the use of membrane separation processes in extended fields, stimuli-responsive membranes with self-regulated performances are designed and fabricated recently. Stimuli-responsive membranes can reversibly alter their physicochemical structures of responsive polymers or functional groups in response to environmental stimuli (e.g., temperature, ion, pH, light, gas, magnetic field, redox and so on), resulting in the changes in pore size and surface properties, and thus the permeability and selectivity are manipulated [4–7]. Stimuli-responsive behaviors are particularly well suited to separate the substances with different sizes using a single membrane for size-selective and charge-based separation [8–10]. Meanwhile, the smart gating membranes can detect and remove of trace heavy metal ions (e.g.,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr(VI)}$ ) from water via surface complexation through easily adding or removing a simple environmental stimulus [11–14]. Furthermore, the self-regulated surface wettability can weaken the affinity between the foulants and the membrane surfaces for reducing or even eliminating the membrane fouling [15–17]. And the switching oil/water wettability between hydrophobicity/oleophilicity and hydrophilicity/oleophobicity enables the as prepared membranes to be used as an oil/water on-off switch for selective oil/water separation [5,18–20].

Stimuli-responsive membranes can be fabricated by various methods. Surface grafting is one of the most popular techniques to incorporate stimuli-responsive polymers on the existing membranes [21–24]. Huang et al. grafted the poly(dimethylaminoethyl methacrylate) (PDMAEMA) chains onto the ethylene vinyl alcohol copolymer (EVAL) membrane by UV-irradiation graft polymerization. The charge-selective membrane can separate the similarly sized proteins of bovine serum albumin (BSA) and bovine hemoglobin (BHB), and the maximum separation factor value is 6.2 at pH 6 [25]. However, the grafted responsive domains often cause a trade-off between the flux and the responsive property, and the surface grafting method is time-consuming and complicated. Alternatively, physical blending before the membrane formation is highly efficient and productive. A variety of amphiphilic copolymers, such as polyethersulfone-*block*-PDMAEMA (PES-*b*-PDMAEMA) [26], polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) [27], poly(methyl methacrylate)-*block*-PDMAEMA (PMMA-*b*-PDMAEMA) [14], polysulfone-*graft*-poly(acrylic acid) (PSf-*g*-PAA) [28] and polyacrylonitrile-*graft*-polyisopropylacrylamide (PAN-*g*-PNIPAm) [29], have been widely used as additives to prepare stimuli-responsive membranes. After being homogeneously dissolved in a solvent, the mixture is often processed into porous membranes via a liquid induced phase separation (LIPS) technique. During membrane formation, the stimuli-responsive chains migrate towards the interfaces of the film/non-solvent and pore/matrix due to their highly hydrophilicity, while the hydrophobic chains entangle with membrane skeletons to firmly tether functional groups [30,31]. Therefore, the as prepared stimuli-responsive membranes often have the desired mechanical properties, pore structure and stability. However, the very fast solidification process of LIPS results in limited control on the microstructures and the responsive properties of the stimuli-responsive membranes.

Recently, a vapor induced phase separation process (VIPS) process was used for fabrication of the thermo-responsive membranes with three-dimensionally interconnected networks of functional gates by self-assembling PNIPAm nanogels on membrane pore surfaces [32,33]. Due to the slow mass transfer rates of VIPS, the microstructures and performances of the membranes can be

efficiently controlled by adjusting the fabrication conditions of the exposure time, the vapor temperature and relative humidity during membrane formation [34–36]. In our previous reports, the casting solutions containing stimuli-responsive groups were synthesized via an *in situ* cross-linking polymerization technique, then they were spread into pH-responsive PSf/PAA and thermo-responsive PSf/PNIPAm membranes by a vapor-liquid induced phase separation (V-LIPS) process [12,37]. Uniform wormlike networks, high flux, reversible response and strong mechanical properties of the porous membranes were obtained simultaneously. However, smart membranes with dual pH- and thermo-responsive performances and open network morphology on the surfaces have not been designed and prepared *in situ* via V-LIPS process till now.

In this work, V-LIPS technique is used for fabrication of dual pH- and thermo-responsive PSf porous membranes. The dope solutions were first synthesized via *in situ* cross-linking polymerization of AA and NIPAm in PSf solutions, then directly proceeded into films. After exposing in water vapor for a predetermined time, they were immersed in a water bath to precipitate. The effect of the weight ratios of AA to NIPAm on the micromorphology, chemical composition, pore structure and hydrophilicity of the as-prepared membranes was characterized in detail. Furthermore, the pure water permeability and the solute rejection of the fabricated membranes at various solution pHs and temperatures were intensively studied. The results in this study provide a valuable guidance for further development of dual stimuli-responsive membranes with satisfactory reversibility as well as desirable separation capability in practical applications.

## 2. Experimental

### 2.1. Materials and reagents

Polysulfone (PSf, Ultrason S 6010) was bought from BASF SE and used after drying at 80 °C overnight. Acrylic acid (AA, 99%), N-isopropylacrylamide (NIPAm, 98%), N,N'-methylenebisacrylamide (MBA, 99%), azobisisobutyronitrile (AIBN, 99%), N,N'-dimethylacetamide (DMAc, 99.8%) and polyethylene glycol (PEG,  $M_w = 0.4, 2$  and 10 kDa), polyethylene oxide (PEO,  $M_w = 100, 300, 600$  and 1000 kDa) were purchased from Aladdin Reagent Co., China and used directly. Hydrochloric acid (HCl, 36–38%) and sodium hydroxide (NaOH,  $\geq 96\%$ ) were supplied by Sinopharm Chemical Reagent Co., Ltd, China.

### 2.2. Membrane preparation

PSf/P(AA-NIPAm) solutions were synthesized via *in situ* cross-linking polymerization and directly proceeded into membranes via V-LIPS process. Typically, PSf (13.5 wt%), PEG with molecular weight of 400 Da (PEG 400, 2 wt%), AA and NIPAm (8.5 wt%) were dissolved in DMAc (76.0 wt%) at 80 °C under protection of nitrogen, then MBA (1 mol% with respect to monomers) and AIBN (2 mol% with respect to monomers) were added into the mixture. Immediately, the cross-linking polymerization was carried out under nitrogen at 80 °C for 10 h, then stopped by exposing in air at room temperature. After bubble releasing, the solution was spread onto a glass plate using a doctor blade with 200  $\mu\text{m}$  air gap and exposed in water vapor (24 °C, 95 %RH) for 8 s and then immersed in a water bath at 30 °C for 24 h to remove solvent and unreacted monomers. During the washing process, the washing water was refreshed every 12 h. The membrane was picked up and dried. The prepared PSf/P(AA-NIPAm) membranes were named as MA-N, in which A and N represents the mass ratio of AA to NIPAm in the solution before polymerization. In addition, the virgin PSf

Download English Version:

<https://daneshyari.com/en/article/6989437>

Download Persian Version:

<https://daneshyari.com/article/6989437>

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