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Effects of fabrication conditions on the microstructures and performances of smart gating membranes with *in situ* assembled nanogels as gates

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ABSTRACT

Smart gating membranes with *in situ* assembled poly(*N*-isopropylacrylamide) (PNIPAM) nanogels as gates are successfully prepared via vapor-induced phase separation (VIPS) with different exposure time periods, temperatures and relative humidities of the water vapor. Effects of the fabrication conditions on microstructures as well as thermo-responsive and mechanical performances of the membranes are investigated. Both the membrane microstructure and the movement of blended PNIPAM nanogels in the membrane forming solution can be controlled by adjusting the fabrication conditions. With increasing the exposure time, the membrane microstructure undergoes a transition from typical liquid-induced phase separation (LIPS) structure (unsymmetrical finger-like porous structure) to typical VIPS structure (symmetric cellular-like porous structure). The critical time periods for the microstructure transition of membranes prepared with vapor temperature and relative humidity of 25 °C/90%, 25 °C/70% and15 °C/70% are about 1.5 min, 2 min and 10 min respectively. The performances of membranes are heavily dependent on the microstructures. The membranes with unsymmetrical finger-like porous structures show large thermo-responsive factor ($R_{39/20}$, the ratio of water flux at 39 °C to that at 20 °C), with the maximum $R_{39/20}$ value being 43.2. All the membranes with symmetric cellular-like porous structures exhibit strong mechanical property and large water flux at 39 °C, which is higher than the volume phase transition temperature (VPTT) of PNIPAM nanogels. The results provide valuable guidance for rational design and fabrication of smart gating membranes with desirable performances.

1. Introduction

Smart gating membranes, which are able to self-regulate their permeation and separation characteristics responding to environmental stimuli, are drawing ever-growing attention from various fields [1–5]. Such smart gating membranes could find myriad potential applications in many fields including water treatment [6–8], controlled release [2,4,9,10], chemical/biological separations [11–15], tissue engineering [16,17] and so on. Therefore, a lot of investigations have been carried out to prepare smart gating membranes with satisfactory performances. Of course, the next goal is to find a feasible approach to achieve mass-production of smart gating membranes for practical applications. However, so far, either the complicated fabrication process or the limited performance such as low flux, poor mechanical property or poor responsive property of the developed membranes makes the prospect of the mass-production of smart gating membranes unclear. From this point of view, the development of an easy way for fabricating smart gating membranes with high flux, strong mechanical property and significant responsive property is of both scientific and technological interests.

Till now, several strategies have been developed to introduce responsive domains into membrane materials for fabrication of smart gating membranes. All the methods for preparing smart gating membranes can be classified into two main classifications according to time order of introduction of responsive domains, *i.e.*, the responsive domains are introduced into membrane materials *after* or *before* the membrane formation [1,18]. To introduce responsive domains into membrane materials *after* the membrane formation, the common ways are to introduce responsive domains onto or into preformed porous membrane substrates by certain

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modification methods including chemical grafting [1–3,7,9,11,12,14,15], physical coating or pore-filling [8,19,20]. Usually, these modification methods retain the good mechanical property of the porous membrane substrates, but the introduced responsive domains onto or into membrane pores cause an inherent conflict between the flux and the responsive property. It means that the content increase of introduced responsive domains brings more significant responsive property and lower flux, and *vice versa*. Meanwhile, the individually operated formation and modification of membranes make the fabrication processes complicated and time-consuming. Furthermore, most of the aforementioned modification methods cannot be scaled up easily at the present stage.

Alternatively, the responsive domains can be first introduced into the membrane-forming materials by either chemical grafting [21,22] or physical blending [18,23,24] *before* the membrane formation. After being homogeneously dissolved into solvent, the modified or blended membrane-forming materials are simply processed into smart gating membranes via liquid-induced phase separation (LIPS). The LIPS process for membrane formation is a mature industrial process, and can be scaled up with currently existed large-scale industrial equipment. However, due to the rapid process of LIPS, the solidification of membrane-forming materials is very fast, which makes it hard to regulate or control the microstructures of smart gating membranes. For instance, although the blended copolymers or nanogels can move towards the interface of the pore/matrix due to its hydrophilic property as well as the Brownian motion, the quick solidification might happen before the movement of responsive domains towards the interface of the pore/matrix completed. As a result, either the fluxes or the responsive properties of smart gating membranes prepared via LIPS are limited [18,21–24]. Meanwhile, the typical structures of membranes prepared by LIPS are the combination of dense skin layer with finger-like macrovoids, which makes the membranes often suffer from poor mechanical properties [25]. So, the application and popularization of LIPS methods for preparing smart gating membranes are still limited by these disadvantages.

Recently, we have proposed a novel and simple strategy for fabrication of smart gating membranes with simultaneous large flux, significant response and excellent mechanical property by constructing responsive nanogels *in situ* assembled on membrane pore surfaces as functional gates via a vapor-induced phase separation (VIPS) process [18]. This approach might be efficient for the mass-production of smart gating membranes with satisfactory performances. However, how will the exposure time of the casting or the wet film to water vapor, and the temperature and relative humidity of the vapor during VIPS process affect the microstructures and performances of the prepared smart gating membranes? These issues are still unclear up to now. It has been reported that the exposure time, the vapor temperature and relative humidity during a VIPS process significantly affect the microstructures and performances of non-responsive membranes [26–28]. Similarly, these parameters during the VIPS process could also affect the microstructures and performances of the smart gating membranes. Moreover, the introduction of responsive domains might bring complexity to the membrane forming solution system [18]. Therefore, systematical investigations of the effects of fabrication conditions during the VIPS process on the microstructures and performances of the smart gating membranes are of scientific importance.

In this study, smart gating membranes with *in situ* assembled poly(*N*-isopropylacrylamide) (PNIPAM) nanogels as gates are prepared via VIPS, and the effects of fabrication conditions during the VIPS processes on the microstructures and performances of membranes are investigated. Exposure of the casting or the wet film to the nonsolvent vapor is the essential difference between the VIPS and LIPS processes, and could make the microstructures and performances of the membranes different [18,27]. Therefore, the exposure time period is precisely adjusted to investigate its effects on the microstructures and performances of the membranes. Except the exposure time period, the temperature and relative humidity of the vapor are the main parameters that can be regulated during the VIPS processes [27]. So, the temperature and relative humidity of the vapor are also varied to investigate their effects on the microstructures and performances of the membranes. The results in this study will provide valuable guidance for rational design and mass-production of smart gating membranes with satisfactory performances.

2. Materials and methods

2.1. Materials

Poly(ether sulfone) (PES, Changchun Jilin Special Plastics) with molecular weight of 40,000 Da was used as membrane materials. *N*-isopropylacrylamide (NIPAM, Sigma-Aldrich) was purified by recrystallization with a hexane/acetone mixture (v/v, 50/50). *N*,*N*'-Methylenebise-*bis*-acrylamide(MBA), ammonium persulfate (APS), *N*-methyl pyrrolidinone (NMP) were reagent grade and used without further purification. Deionized (DI) water (18.2 MΩ, 25 °C) produced from a Milli-Q Plus water purification system (Millipore) was used throughout the work.

2.2. Preparation of nanogels and membranes

The PNIPAM nanogels were prepared according to our previously reported method [18]. Firstly, monomer NIPAM, crosslinker MBA and initiator APS were mixed with a molar ratio of 100:5:2, and dissolved in 200 mL DI water. The molar concentration of NIPAM was constant at 0.1 mol L^{-1}. The monomer solution was bubbled with nitrogen gas for 30 min to remove the dissolved oxygen, and then was heated to 70 °C to initiate the polymerization. The precipitation polymerization was carried out in a water bath at 70 °C for 4 h. The resultant PNIPAM nanogels were thoroughly purified by centrifugation at 8000 rpm and then re-dispersed in DI water to remove the residual unreacted components. The purification process was repeated for 3 times. The purified PNIPAM nanogels were freeze-dried at −35 °C for 48 h and reserved for further use. Dynamic light scattering (DLS, Zetasizer Nano ZS90, Malvern) was used to test the average diameter of PNIPAM nanogels in water. The hydrodynamic diameter of the PNIPAM nanogels in water is 820 nm at 25 °C and 400 nm at 44 °C.

Smart gating membranes with nanogels as gates were fabricated from nanogel-contained membrane-forming solution via VIPS. The solvent NMP, PES and freeze-dried PNIPAM nanogels were mixed with a mass ratio of 100:17.5:3.0 at 20 °C. The viscosities of the solutions were tested by a viscometer (DV2T, Brookfield). After full agitation and deaeration, the homogeneous membrane-forming solution was casted onto a glass plate with a casting machine (FM-2, Ningbo Jiangbei) to get the casting or wet film with a thickness of 200 μm. The casting film together with the glass plate was then put into a constant-temperature and constant-humidity vapor chamber (TH-PE-100, JEIO), in which the temperature and the relative humidity of water vapor could be maintained constantly. To investigate the effects of process conditions on the membrane microstructures, the residence time of the casting or the wet film exposed to the water vapor in the vapor chamber was varied from 0 min to 20 min, while the vapor temperature was 15 °C or 25 °C, and the relative humidity was 70% or 90%. Subsequently, the casting or wet film together with the glass plate was immersed in a water bath at 22 °C to achieve sufficient