



Achieving persistent high-flux membranes via kinetic and thermodynamic synergistic manipulation of surface segregation process



Mingrui He^{a,b}, Runnan Zhang^{a,b}, Yanan Liu^{a,b}, Lin Fan^{a,b}, Qi Zhang^{a,b}, Yanlei Su^{a,b},
Zhongyi Jiang^{a,b,*}

^a Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

ARTICLE INFO

Keywords:

Membrane technology
Surface segregation
Surface enrichment
Thermodynamic manipulation
Kinetic manipulation

ABSTRACT

Persistent high-flux membranes were fabricated via kinetic and thermodynamic synergistic manipulation of surface segregation process. Poly (ether sulfone) (PES) was utilized as the bulk membrane material, poly (N-vinyl pyrrolidone-*alt*-maleic anhydride)-*b*-poly(styrene) (P(NVP-*alt*-MAH)-*b*-PS) with polyethylene glycol (PEG) was utilized as the precursor of surface segregation modifiers (SSMs). In casting solutions, the SSMs were in-situ synthesized through the alcoholysis reaction between the anhydride groups in P(NVP-*alt*-MAH)-*b*-PS and the hydroxyl groups in PEG, and then the membranes were fabricated with the non-solvent induced phase separation of PES and the surface segregation of the SSMs. The high mole ratio of hydrophilic/hydrophobic segments and adjustable crosslinking degree of the SSMs afforded the sufficient surface enrichment of the hydrophilic segments in the SSMs, as a result, the coverage of PEG segments on the membrane surfaces reached as high as 40.0 at%. Meanwhile, the strong interactions between the SSMs and PES and the high molecular weight of the SSMs afforded the durable surface enrichment of the SSMs, as a result, the water contact angle and the O/C ratio of the membrane surfaces were nearly unchanged after scoured by water for 30 days. Moreover, the crosslinked SSMs interfered and delayed the solidification of PES, endowing the membranes with higher porosity and bigger pore sizes. Accordingly, the membranes displayed persistent high-flux of $230 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ in ternary-circle ultrafiltration experiment.

1. Introduction

As a green, efficient membrane separation technology, ultrafiltration (UF) is widely used in water treatment [1,2]. However, the upstream feed solutions of UF usually contains diverse kinds of foulants, which may adsorb or deposit on membrane surfaces and block membrane pores in the long-term utilization, leading to the significant decline of membrane permeation fluxes and life span [3–5].

Persistent high-flux is the everlasting pursuit of separation membranes, which is reflected by the initial high-flux and persistent anti-fouling performance. The rational design and construction of hydrophilic membrane surfaces is a well-recognized avenue [4,6,7]. Surface segregation is an in-situ modification method, which can create uniform efficacious brush layers to acquire the 3D modification of membranes with amphipathic surface segregation modifiers (SSMs) [1,8–10]. The sufficient and durable surface enrichment of the hydrophilic segments in SSMs is the critical target of surface segregation, which governs the modification efficiency of membranes. The sufficient surface

enrichment is accomplished in membrane formation. During membrane formation, the diffusion of non-solvents forms steep concentration gradients near membrane surfaces, which causes the shrinkage and solidification of bulk membrane materials (BMMs) driven by solubility difference as well as the surface segregation of SSMs driven by chemical potential difference [11]. At the beginning stage of membrane formation, there was large space among polymer networks, the resistance of surface segregation is low, so the SSMs continuously move towards, or even out of membrane surfaces rapidly. With the shrinkage and solidification of BMMs, the space among polymer networks decrease considerably and the chain entanglement is aggravated, which causes the increase of segregation resistance. The segregation speed gradually decreased to almost zero when the shrinkage and solidification of BMMs tends complete. In theory, if the speed of the surface segregation is much faster than that of the solidification, most of SSMs are likely to escape from membrane surfaces, which is called oversegregation [12], on the contrary, if the speed of the surface segregation is much slower than that of the solidification, most of SSMs are likely to be buried

* Corresponding author at: Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.
E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

inside membranes, which is called undersegregation [13]. Ideal surface segregation falls in between oversegregation and undersegregation with hydrophilic segments exactly stretching out of membrane surfaces and hydrophobic segments exactly entrapped inside membranes, which ensures the sufficient surface enrichment of the hydrophilic segments in SSMS. The durable surface enrichment is examined in membrane operation. During operation, the surface segregation of SSMS do not terminate completely, SSMS are still likely to elute from membrane surfaces driven by chemical potential difference and physical shear force, which is called leaching out [14]. Obviously, the leaching out should be avoided.

The strategy to achieve the durable surface enrichment in membrane operation seems quite simple, because the leaching out is a slow process primarily controlled by thermodynamics, which can be alleviated by lowering the chemical potential difference of SSMS near membrane surfaces, such as the enhancement of interactions between SSMS and BMMs [14–16] or the increase of molecular weight of SSMS [17,18]. However, the strategy to achieve the sufficient surface enrichment during membrane formation proves rather complicated, because the surface segregation in membrane formation is a fast process primarily controlled by kinetics, which is easily affected by multiple factors. On one hand, the degree of surface segregation should be appropriately manipulated, avoiding the tendency of oversegregation or undersegregation; on the other hand, the undesired surface enrichment of hydrophobic segments in SSMS should be prevented. The former issue have been extensively investigated with the results that the decrease of hydrophilic/hydrophobic ratio of SSMS [17,19] and the increase of the crosslinking degree of SSMS [18] could increase the segregation resistance and decrease the segregation speed, whereas the latter issue remains an open problem: Even though SSMS were exactly enriched on membrane surfaces via kinetic manipulation of surface segregation, the surface coverage of target hydrophilic segments was not high enough, all less than 35 at% as reported in the existing literatures [17–21]. The surface segregation during membrane formation is mainly governed by kinetics, parts of SSMS on membrane surfaces did not win enough time to reach thermodynamic equilibrium, and thus the orientations of the SSMS were often in a random state: some hydrophilic segments were buried inside membranes and some hydrophobic segments stretched out of membrane surfaces, which hindered the sufficient enrichment of hydrophilic segments. Because of the random orientation, the surface enrichment ratio of hydrophilic/hydrophobic segments was closely associated with the hydrophilic/hydrophobic ratio of SSMS. For instance, in Zhao's work, low hydrophilic/hydrophobic ratio was utilized to alleviate oversegregation, the surface coverage of SSMS reached 66.4%, but the surface coverage of hydrophilic segment was merely 20.0% [19]. Increasing the surface coverage of hydrophilic segments becomes an important research task. Therefore, this study aimed at the kinetic manipulation of surface segregation to achieve the sufficient surface enrichment of the hydrophilic segments and the thermodynamic manipulation of surface segregation to achieve the durable surface enrichment through the rational design of SSMS. In regard to kinetics, the combination of high hydrophilic/hydrophobic ratio and adjustable crosslinking degree of SSMS was adopted to pursue ideal surface segregation. The high hydrophilic/hydrophobic ratio could reduce the surface enrichment of hydrophobic segments caused by the non-thermodynamic equilibrium, and the adjustable crosslinking degree could alleviate the oversegregation. In regard to thermodynamics, the increased molecular weight caused by crosslinking could contribute to the durable stability of SSMS.

In details, the SSMS with high hydrophilic/hydrophobic ratio were in-situ synthesized though the alcoholysis reaction between the anhydride groups in the poly (maleic anhydride-*alt*-N-vinyl pyrrolidone)-*b*-poly(styrene) (P(NVP-*alt*-MAH)-*b*-PS) and the hydroxyl groups in PEG. According to the different addition ratio of two reactants, the SSMS P (NVP-*alt*-MAH)-*b*-PS/PEG processed different crosslinking degree. Through kinetic and thermodynamic synergistic manipulation of

surface segregation process, the membranes were rendered remarkable surface enrichment of the hydrophilic segments in the SSMS and exhibited persistent high flux of $230 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$.

2. Experimental

2.1. Materials

PES in flake form (6020 P) was purchased from BASF Co. (Germany) and was dried at 75 °C for 24 h before utilization. Styrene, NVP and PEG with the molecular weight of 2.0 kDa were purchased from Aladdin Industrial Co. (China). DMF, MAH and Azoisobutyronitrile (AIBN) were purchased from J & K Scientific Ltd. (China). Bovine serum albumin (BSA) was purchased from Institute of Hematology, Chinese Academy of Medical Science (Tianjin, China). Deionized water was produced by Elix[®] Essential 5, which was purchased from Merck Millipore Co. (America). A series of dextran with different molecular weight (Mw 70, 150, 250 kDa) was purchased from J & K Scientific (China).

2.2. Precursor synthesis and characterization

The synthesis of the SSM precursor P(NVP-*alt*-MAH)-*b*-PS (the precursor for short below) was achieved by free radical polymerization initiated by AIBN. The monomer molar ratio of NVP, MAH and SM was 1:1:4, respectively. MAH (1961.2 mg, 0.02 mol) and NVP (2222.8 mg, 0.02 mol) were dissolved in DMF (100 mL) and then put into a three-necked round bottom flask. The flask was placed in an oil bath under the atmosphere of nitrogen at temperature of 70 °C. After the evacuation of oxygen for 30 min, AIBN (209.2 mg) was added into the flask. After a reaction time of 3 h, SM (8332 mg, 0.08 mol) was added into the flask. After an additional reaction time of 8 h, the flask was filled with oxygen to scavenge free radicals. In order to remove unreacted monomers and oligomers, the obtained copolymers solution was dialyzed with the molecular weight cut-off of 6000 kDa in DMF for 96 h. At last, the solution was completely dried in an oven of 120 °C until reaching constant weight.

The resulting precursor was characterized by Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and gel permeation chromatography (GPC). The characteristic functional groups of the precursor were verified with the FT-IR instrument (VERTEX 70, Bruker Co., Germany) in the transmission mode with air as the background. The chemical composition of the precursor was acquired with the XPS instrument (PHI-1600, Perkin-Elmer Co., USA) using Mg K α (1254.0 eV) as radiation source with the take-off angle of photoelectron at 90°. The molecular weight and distribution of the precursor was measured with the GPC instrument (Waters1515, Waters Co., USA).

2.3. Membrane preparation

Asymmetric PES ultrafiltration membranes were prepared by NIPS with the in-situ reaction and surface segregation of the SSMS. The formulations of the casting solutions were presented in Table 1. The contents of PES and PEG were fixed at 16.0 wt% and 6.0 wt%, respectively, and the contents of the precursor varied from 0.0 to 1.0, 1.5, 2.0,

Table 1
The formulations of the casting solutions.

Membrane	PES (g)	PEG (g)	Precursor (g)	DMF (g)
PES/PEG	1.60	0.60	0.00	7.80
PES/PEG/Precuorsr-1.0 wt%	1.60	0.60	0.10	7.70
PES/PEG/Precuorsr-1.5 wt%	1.60	0.60	0.15	7.65
PES/PEG/Precuorsr-2.0 wt%	1.60	0.60	0.20	7.60
PES/PEG/Precuorsr-2.5 wt%	1.60	0.60	0.25	7.55
PES/PEG/Precuorsr-3.0 wt%	1.60	0.60	0.30	7.50

Download English Version:

<https://daneshyari.com/en/article/4988700>

Download Persian Version:

<https://daneshyari.com/article/4988700>

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