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Remarkable pH-sensitivity and anti-fouling property of terpolymer blended polyethersulfone hollow fiber membranes

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ABSTRACT

This work presents a detailed study on the pH sensitivity of polyethersulfone (PES) hollow fiber membrane (HFM) modified by blending an amphiphilic terpolymer poly(styrene–acrylic acid–N-vinylpyrrolidone) (P(St–AA–NVP)), the HFM exhibits a pH-responsive behavior with very large water flux change as the pH value change, from nearly 38.64 to 0.64 ml/(m^2 h mmHg). Meanwhile, the influence of the occurred macro- and micro-phase separation on water contact angle, pH sensitivity, and anti-fouling property was investigated. X-ray photoelectron spectroscopy analysis revealed the enrichment of the hydrophilic segments of the terpolymer at the membrane surface. A rough surface resulted from the poor miscibility of the blend was observed, and it was proved that the phase separation would increase the pH sensitivity. Furthermore, the ultrafiltration experiments indicated that the phase separation had great effect on the pure water flux but little influence on the protein anti-fouling property after the blending of the terpolymer; and the modified membrane showed good protein anti-fouling property.

1. Introduction

Polymeric membranes have been widely used in blood purification, water treatment, tissue and gene engineering, and so on [1–3]. To approach these different applications, numerous researches had been carried out to explore the modification of polymeric membranes [4–6]. The modified membranes with stimuli-responsivity, which exhibited abrupt property change in response to small change in the external stimuli such as temperature, pH, ionic and solvent composition of the media, concentration of specific chemical species, electric field, and photo-irradiation [7,8], provided a variety of new abilities to the porous membranes and broadened the application fields. Among the stimuli-responsive membranes, pH-sensitive membranes as a novel and powerful technique with pH reversible “switchable” properties, have been received a rapidly increasing interest in recent years [9–13]. For the practically unlimited possibilities to design pH-responsive functional polymer systems, polymers containing carboxyl and pyridine groups are the most important materials or building blocks for such “smart” membranes [14].

It is convenient to prepare pH-sensitive flat-sheet membrane (FSM); thus, most of the studies focused on FSMs. Pore-filled method was extensively investigated to prepare pH-sensitive FSM, and could change microfiltration or ultrafiltration membrane to nanofiltration membrane. Grafting method is another good way to prepare pH-sensitive membranes. Both the pore-filled and grafting methods are easy to be used for the preparation of FSMs, and the mechanisms of these pH-sensitive membranes had also been investigated [15–18]. However, the pore-filled and grafting methods are difficult to be used for fabricating and modifying HFM; and few studies on pH-sensitive HFM were reported and the flux change was not very larger [19,20]. Blending is a convenient method to prepare any kinds of membranes including HFM as reported in our earlier study [21]. Due to the large surface/volume ratio, the recent development of pH-sensitive HFM might highlight the adaptability of the stimuli-responsive membranes to the whole flux control, selective sieving process and large-scale separation devices [14,22].

Poly(acrylic acid) (PAA) is an important polyelectrolyte and pH-sensitive material used for preparing pH-sensitive membranes. Its reversible swelling-shrinking behavior is caused by the transformation between the de-ionization form (–COOH group) and the ionization form (–COO^- group) at pH values around a pK_a of about 4.7 [23]. In our recent studies [21,24], a random copolymer poly(acrylonitrile–acrylic acid) was blended into polyethersulfone (PES) to prepare pH-sensitive HFM. The blended PES HFM showed evident pH-sensitivity and pH reversibility; and we also

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found that the electroviscous effect played an important role on the pH-sensitivity. Zou et al. [25] developed multi-functional HFM, a random terpolymer of poly(methyl methacrylate–acrylic acid–vinyl pyrrolidone) was blended with PES to prepare HFM, and the HFM showed good pH-sensitivity and anti-fouling property. It was found that the fluxes under acid conditions were over 10 times larger than those under basic conditions, and the electroviscous effect was also observed. However, the electroviscous effect mechanism of the HFM had not been analyzed.

In the studies mentioned above, it was also found that the miscibility between the matrix polymer and the pH-sensitive amphiphilic copolymer would influence the performance of the HFM. To decrease the effect of phase separation, partially miscible hydrophobic segment was chosen to synthesize the amphiphilic copolymer. The aim of the present work is to develop a new amphiphilic copolymer to modify PES membranes, and to investigate the factors that affect the pH sensitivity of the PES HFM, and the influence of the occurred complex (macro and micro) phase separation on the HFM performance [26]. Polystyrene, with a Hansen solubility coefficient $\delta t = 17.52\,(\mathrm{MPa})^{1/2}$, showed the poorest miscibility with PES ($\delta t = 21.96\,(\mathrm{MPa})^{1/2}$) compared with poly(acrylonitrile) ($\delta t = 25.27\,(\mathrm{MPa})^{1/2}$) and poly(methyl methacrylate) ($\delta t = 22.69\,(\mathrm{MPa})^{1/2}$) [27]; the miscibility also have been proved by using the cloud point measurements, all of these showed similar results.

In the present work, polystyrene was chosen as the hydrophobic segment to synthesize a new pH-sensitive amphiphilic copolymer of poly(styrene–acrylic acid–N-vinylpyrrolidone) (P(St–AA–NVP)); the PAA chains in the copolymer provided hydrophilicity, pH sensitivity, reactivity and anti-fouling property [18,28]; the PVP chains could improve the hydrophilicity [29,30] and blood compatibility [29–32]. Additionally, numerous attempts have been made to explain the factors that might affect the pH sensitivity of the HFM, especially the electroviscous effect. Furthermore, the effect of the formed macro- and micro-phase separation structures on water contact angle, pH sensitivity, and anti-fouling property was also explored.

2. Experimental

2.1. Materials

Monomers acrylic acid (AA, Kelong Chemical Reagent Inc., Chengdu, China), styrene (St, Kelong Chemical Reagent Inc., Chengdu, China) and N-Vinylpyrrolidone (NVP, obtained from Alfa Aesar) were used to synthesize the functional terpolymer; all of them were distilled under vacuum. 2,2′-azobisisobutyronitrile (AIBN) was the initiator and 1,4-dioxane was the solvent; and both were purchased from Chengdu Kelong Chemical Reagent Company. Polyethersulfone (PES, Ultrason E6020P, BASF, Germany) was used to prepare the membranes and dried at 80 °C for 12 h before use. Bovine serum albumin (BSA, fraction V) was obtained from Sigma Chemical Co., and used for ultrafiltration experiments. Polyethylene glycol (PEG, Mw = 10,000), and N,N-dimethylacetamide (DMAc) were purchased from Chengdu Kelong Chemical Reagent Company. All the other reagents are of analytical grade and used without further purification.

2.2. Synthesis and characterization of P(St–AA–NVP) functional terpolymer

The terpolymer was synthesized by radical solution polymerization. Monomers of St, AA and NVP (The ratio is 4:4:2) were dissolved in 1,4-dioxane with the total monomer concentration of 30 wt.%. The initiator, AIBN was introduced into the mixed solution at 0.3 wt.% of the total monomer weight, and then the solution was stirred continuously until all the monomers were completely dissolved. After passing nitrogen for 15 min, polymerization was carried out in air tight equipment at 75 °C for 24 h. Then the product was washed several times with double distilled water and ethanol respectively to remove the residual monomers, initiator, some homopolymers, and solvent thoroughly, which were confirmed by pH test and UV scanning. The obtained terpolymer was dried completely at 60 °C in a vacuum oven for over 72 h.

Fourier transform infrared (FTIR) analysis was carried out to confirm the chemical groups of the synthesized terpolymer. The FTIR spectrum was obtained using a FTIR spectrometer (Nicolet 560, America). To prepare the sample, the P(St–AA–NVP) was dissolved in 1,4-dioxane (boiling point 101 °C); and then cast onto a KBr plate, and dried by an infrared light to remove the 1,4-dioxane.

Differential scanning calorimetry (DSC) measurements were used to measure the glass transition temperature of the synthesized terpolymer, which were conducted on a computer control electronic universal testing machine KLIII-5. Average solid sample weight of 8.6 mg was tightly sealed onto the DSC pans. The first scan was run to 180 °C to erase the previous thermal history at a heating rate of 30 °C/min, and then the sample was quenched to 50 °C to start the second scan. The glass transition temperature (T_g) was scanned at a temperature ranging from 50 °C to 200 °C at a heating rate of 10 °C/min under nitrogen flow (30 psi).

Monomer contents in the terpolymer were determined by measuring carbon (C), hydrogen (H) and nitrogen (N) contents in the terpolymer by elemental analysis (CARLO ESRA-1106 elemental analyzer (Milan, Italy)). The mole ratios of St, AA and NVP repeat units were calculated from the content of each atom. Then the mole ratio was transferred to weight ratio.

GPC measurement, which is based on the liquid chromatography analysis using an aqueous gel permeation column, was performed by using the PL220 GPC analyzer (Britain), and N,N-dimethyl formamide (DMF) was chosen as the eluent.

2.3. Hollow fiber membrane preparation

The HFM was fabricated by the dry-wet spinning technique as described in our earlier report [21]. The HFM prepared with different terpolymer amounts were termed HFM-0, HFM-0.4, HFM-0.8, HFM-1.2, and HFM-1.6, respectively (as shown in Table 1). The HFM filters were prepared by employing epoxy resin as the potting material, with an effective area of about 120 cm^2.

For the characterization of the surface property of the porous membrane, flat-sheet membranes (FSMs) with the same proportions as the HFMs were prepared by a phase inversion technique at room temperature, and were termed FSM-0, FSM-0.4, FSM-0.8, FSM-1.2, and FSM-1.6, respectively (compositions are shown in Table 1).

2.4. Characterization of the P(St–AA–NVP) blended membranes

An X-ray Photoelectron Spectroscopy (XPS; KRATOS XSAM800, Britain) instrument was used to determine the surface composi-

Table 1
Compositions of the casting solutions for preparing PES/P(St–AA–NVP) membranes: hollow fiber membrane (HFM) and flat-sheet membrane (FSM).

No.	PES (wt.%)	Terpolymer (wt.%)	DMAC (wt.%)
HFM-0/FSM-0	20	0	80.0
HFM-0.4/FSM-0.4	20	0.4	79.6
HFM-0.8/FSM-0.8	20	0.8	79.2
HFM-1.2/FSM-1.2	20	1.2	78.8
HFM-1.6/FSM-1.6	20	1.6	78.4