



Preparation, characterization and application of functional polyethersulfone membranes blended with poly (acrylic acid) gels

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ABSTRACT

In this paper, we provide a simplified method to prepare functional polyethersulfone (PES) membranes with pH sensitivity and ion-exchange capacity by blending cross-linked poly (acrylic acid) (PAA) sub-micrometer-scale gels. The PAA gels were synthesized through the solution polymerization of acrylic acids in dimethylacetamide (DMAC) under strong agitation, the size of the gels ranged from about 250 to 3000 nm. With the increase of the agitation rate, the gel size increased. The PAA gel solution can be directly blended with PES solution (using DMAC as the solvent) to prepare membrane using a phase separation technique. After blending the PAA gels, the morphology of the PES membrane was substantially altered; and the finger-like structure became a sponge-like structure. The blended PES membranes showed evident pH sensitivity and pH reversibility; and the pH-valve effect was observed at pH between 3 and 8. With the increase of the gel size, the pH sensitivity increased; and with the increase of the gel amount blended in the membrane, the water flux increased under acid conditions. The permeability results suggested that the flux of acidic amino acid solution was higher than basic amino acid solution. The Cu²⁺ ion-exchange experiment indicated that the membranes could bind metal ions, and had potential to be used as ion-exchange membranes.

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1. Introduction

Polyethersulfone (PES) is one of the most important polymeric materials. PES shows outstanding oxidative, thermal, and hydrolytic stability as well as good mechanical and film-forming properties. The polymer has been widely used in membrane separation for various applications, such as microfiltration and ultrafiltration (UF) process in the fields of biomedicine, food, hemodialysis, plasma separator, and water purification, etc. [1–4]. With respect to improved membrane properties, modifications of the pore structure and of the surface physical-chemistry had been addressed in several previous efforts. For PES, such modifications can be achieved by additives to the casting solution and by changes in the conditions during the membrane formation process (NIPS) as well as by combinations thereof [5–7]. Another alternative is offered by surface modifications of the membrane after preparation [8–10]. Our interest is focused on the functionalization of the PES membranes by endowing with pH sensitivity for advanced separation.

Several researchers have reported the pH-sensitive membranes. Childs and coworkers [11] provided a new type of membrane composed of a microfiltration substrate and a pore-filling polyelec-

trolyte produced by UV induced grafting of 4-vinylpyridine onto polyethylene and polypropylene microfiltration membranes. The membranes showed an outstanding pH-valve effect and the capability of rejecting small inorganic ions in the process of reverse osmosis. Thereafter, the effect of the cross-linking of the polyelectrolyte on the flux and separation, the effect of polyelectrolyte composition on the membrane performance, and the effect of gel layer thickness on the salt rejection performance were investigated [12–15]. Hu and Dickson [16] developed the pore-filled pH-sensitive membranes by *in situ* cross-linking poly (acrylic acid) inside poly (vinylidene fluoride) hydrophobic microporous substrate membranes, and the membranes demonstrated a rapid and reversible response of flux to environmental pH as the pH was changed between 2.5 and 7.4. M'Bareck et al. [17] reported a simplified, efficient and economical method for fabricating ion-exchange ultrafiltration membranes. To obtain these membranes by the phase inversion method, polysulfone (PSf) and poly (acrylic acid) (PAA) were separately dissolved in dimethylformamide (DMF), and then the two solutions were mixed in desired proportions; however, some of the PAA was eluted during the preparation process, and no filtration process was mentioned in the study. Wu and coworkers [18] developed the pH and temperature sensitive membranes by blending with nanoparticles of poly(N-isopropylacrylamide-co-methacrylic acid). The nanoparticles were synthesized by aqueous dispersion polymerization. And the nanoparticles should be puri-

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Table 1

The composition of the PAA/PES blended membranes.

Membranes no.	Mass fraction of PAA in the casting dopes (wt.%)	Mass fraction of PAA in the membranes (wt.%)	Agitation rate (rpm) of PAA gels synthesized
M-0	0	0	–
M-2-1	2	9.4	100
M-6-1	6	23.0	100
M-10-1	10	32.4	100
M-10-5	10	32.4	500

fied by membrane dialysis and be dried before blending in the membranes. To avoid the leakage of the nanoparticles from the membrane surface, the membranes should be coated with polyelectrolyte layers. These problems restricted the wide application of this method, such as preparation of hollow fiber membrane.

PAA is one example of the attractive pH-sensitive material, and is characterized by an ionizable hydrophilic property. Its reversible swelling–shrinking behavior is caused by the transformation between the deionization form (COOH group) and the ionization form (COO[−] group) at pH values around a pKa of about 4.7 [19]. However, when PAA was blended directly with other polymer as described in the literature [17], the elution of PAA was unavoidable due to its water dissolubility.

In this study, we provide an easy method to prepare pH-sensitive and ion-exchange PES membranes by blending cross-linked PAA sub-micrometer-scale gels with PES in a same solvent. The cross-linked PAA gels were synthesized in dimethylacetamide (DMAC) solution, and then the gel solution was blended with PES/DMAC solution. By using a phase inversion method, PES–PAA gel blended membranes were prepared. In this case, the cross-linked PAA gels were incorporated into the PES substrate. The microgels would not leak from the membranes, because the size of the pores in the dense skin layer of the membranes was smaller than the gels. The pH-valve effect on the membranes and the application of the membranes, such as the ion-exchange capacity and the permeability control of amino acids, were also investigated.

2. Experimental

2.1. Materials

Acrylic acid monomer (AA, Kelong Chemical Reagent Inc., Chengdu, China) was used to synthesize the cross-linked poly (acrylic acid) (PAA) gels. N,N-methylene-bis (acrylamide) (MB, Kelong Chemical Reagent Inc., Chengdu, China) was the cross-linker. Azo-bis-isobutyronitrile (AIBN, Shisihewei Chemical Reagent Inc., Shanghai, China) was the initiator. Polyethersulfone (PES, Ultrason E6020P, CAS Number: 25608-63-3, BASF Aktiengesellschaft) was used to prepare the membranes. Polyethylene glycol (PEG-600, Kelong Chemical Reagent Inc., Chengdu, China) was used as the additive to improve the flux of the membrane. N,N-dimethylacetamide (DMAC, Kelong Chemical Reagent Inc., Chengdu, China) was used as the solvent. Copper sulfate (CuSO₄, Kelong Chemical Reagent Inc., Chengdu, China) was used for the measurement of ion-exchange capacity. L-Aspartic acid (Asp) and L-lysine (Lys) (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used as amino acid models in ultrafiltration process.

2.2. Synthesis of cross-linked PAA gels

The cross-linking of PAA was carried out by free radical polymerization of AA in DMAC. A mixture of AA (25.29 wt.%), MB (4.71 wt.%), and AIBN (0.3 wt.%) in DMAC were placed in a glass reactor, and bubbled with nitrogen. The polymerization was carried out at 65 °C for 14 h to complete the reaction, and the agitation speed was con-

trolled at 100, 300 or 500 rpm. The cross-linked PAA gels were characterized by a Nano-zatasizer (Zetasizer Nano ZS model number: ZEN3600, Malvern Instruments, UK) and a scanning electron microscopy (SEM; JSM-5900LV, JEOL, Japan). For the SEM observation, aether was added in the gel solution, and then the solution was centrifugated at 8000 rpm, and then was freeze-dried. The gel sample was attached to the sample supports and coated with a gold layer.

2.3. Membrane preparation

PES was dissolved in DMAC, and then required amounts of the cross-linked PAA gels and PEG were added, PEG was used as the porous reagent here. The mass fraction of PES in all the casting solutions is 16%, and that of PEG is 4%. Then the solution was stirred for 10 min to form the casting dope. After vacuum degassed, the casting solution was prepared into membranes by spin coating coupled with a liquid–liquid phase separation technique [20–23] at room temperature, with the double distilled water as non-solvent. The membranes were rinsed with double distilled water thoroughly to remove the residual solvent, and stored in double distilled water till use. The thickness of the membrane was 65 ± 5 μm. The composition of the blended PES membranes with PAA gels is shown in Table 1.

2.4. Determination of ion-exchange capacity (IEC)

To measure the IEC, a membrane sample was alternately equilibrated by 0.1 M HCl and 0.1 M NaOH solutions for a couple of times, and washed by double distilled water in between. Afterward, enough NaOH solution permeated through the membrane sample at 50 kPa, using the apparatus as described in Section 2.6, and followed by a thorough washing with double distilled water. Then, the sample was permeated by HCl solution at 50 kPa, with the concentration and the volume were adjusted to contain about twice the HCl required for theoretical IEC, which was calculated according to the AA mass in the sample. The sample was removed from the apparatus and washed by double distilled water. The permeated HCl solution was then titrated with a standard NaOH solution (0.01 M) using a pH meter as the indicator. HCl and NaOH solutions permeated through the membranes sample thoroughly, and the amount of the solutions remained in the microvoid of the membranes or in the filter was very small. We have also measured the IEC of the PES membrane without PAA gels, and the data were considered when we calculated the IEC of the membranes. The IEC is expressed in the units of milliequivalents of proton atoms per gram of the dry membrane and was calculated by [11]:

$$\text{IEC (mequiv./g)} = \frac{V_{\text{HCl}}N_{\text{HCl}} - V_{\text{NaOH}}N_{\text{NaOH}}}{m_c} \times 1000 \quad (1)$$

where V_{HCl} and V_{NaOH} are the volumes of the HCl and NaOH solutions, respectively. N_{HCl} and N_{NaOH} are the normalities of the HCl and NaOH solutions, respectively.

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