Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Membrane Science 274 (2006) 200–208
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

The preparation and characterization of novel charged polyacrylonitrile/PES-C blend membranes used for ultrafiltration

Meng Wang [a], Li-Guang Wu [b,*], Jian-Xiong Mo [b], Cong-Jie Gao [a,b]

[a] *Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China*
[b] *National Engineering Research Center for Liquid Separation Membrane, Hangzhou 310012, China*

Received in revised form 9 May 2005; accepted 14 May 2005
Available online 27 December 2005

Abstract

2-Acrylamido-2-methylpropane-sulfonic acid (AMPS) was incorporated into polyacrylonitrile by water-phase precipitation copolymerization successfully. The chemical structure, molecular weight and chemical composition of the synthesized copolymer were characterized by IR, viscosity measurement and elemental analysis, respectively. Furthermore, blends of phenolphthalein poly(ether sulfone) (PES-C) and the synthesized copolymer with different composition dissolved in dimethylformamide (DMF) were used to prepared the ultrafiltration membranes by means of classical phase inversion process. And then, the effect of the blend composition on the hydrophilicity, electrical properties, morphologies and permeation properties of the blend membranes was investigated elaborately. The static water contact angle of the blend membrane surface decreased from $78.7 \pm 0.9^\circ$ to $42.6 \pm 3.5^\circ$ with the increase of PAN-co-AMPS from 0 to 20%. It was found that salt retention properties of the blend membranes were influenced intensely by both the content of the charged copolymer and the pH of feed solution. In addition, FESEM images of membrane surface and cross-section displayed that pore size decreases, the top layer became thicker and the finger-like macrovoids disappeared gradually as the PAN-co-AMPS was added. As a result, the water flux is decreased from 230 to 40 L/m^2 h and rejection of PEG20000 and PEG35000 was increased from 0.129 to 0.7389, and 0.5528 to 0.91, respectively (as measured at 100 kPa).

Keywords: Ultrafiltration; Charged membrane; Blends; Phenolphthalein poly(ether sulfone); Electrical properties

1. Introduction

Polymer blending is of great interest because it is an important alternative to obtain new polymeric materials with designed properties, less complicate than developing new polymerization and the least expensive [1]. Therefore, from academic and technological point of view, many studies on the blend membranes have also been carried out. To sum up, there are two types of blend membranes [2]: one in which both polymers are to remain in the end-use, such as PAN/PVDF [3], CA/SPSF [4], etc. and another in which one polymer is removed as a pore former to produce porous membranes, such as Regenerated cellulose/PEG [5], Chitosan/synthetic polymer [6], etc.

Polyacrylonitrile has been successfully applied as membrane material in many fields, such as dialysis, ultrafiltration, and pervaporation. In order to meet different requirements imposed by different membrane applications on membrane materials, copolymerizing vinyl monomers such as maleic anhydride [7], α-allyl glucoside [8], glycidyl methacylate [9], methacrylic acid [10], *N*-vinylimidazol [11], 3-sulfoproyl acylate potassium salt [12], hydroxyethyl methacrylate [13], vinyl pyrrolidone [10], acrylic acid [14], acrylamide [15], vinylchloride [16] with acrylonitrile has been used to improve the pervaporation properties, water flux, fouling reducing, biocompatibility, and even for enzyme immobilization. However, as far as we know, there was few report concerning preparation of the charged acrylonitrile-based polymeric membrane though some fragmentary data [12] about synthesize of the charged acrylonitrile-based copolymer was reported. It is well known that charged polymers can not only change the hydrophilicity of membranes which can reduce fouling and improve biocompatibility, but also provide charges on the membrane surface and pore wall which is another effective factor on the retention of membranes in filtration process besides steric effect of the pores. For example, Zhao et al. [17]

* Corresponding author. Tel.: +86 571 8893 5365; fax: +86 571 8886 8427.
E-mail address: wu_liguang@hotmail.com (L.-G. Wu).

0376-7388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2005.05.035

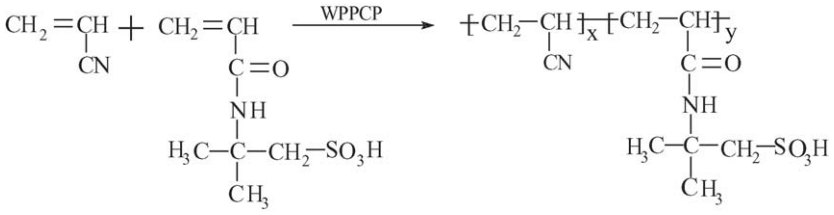

Fig. 1. The preparation route of PAN-co-AMPS.

prepared charged carboxymethyl chitosan/PES composite MF membrane, which may resist protein fouling at high pH applications and separate protein by adsorption at low pH applications. Bowen et al. [18] investigated the retention of salts with charged PEI/SPEEK UF membranes and the rejection observed was as high as 60%.

Hence, in the present work, the charged acrylonitrile-based polymer, PAN-co-AMPS, was synthesized through the copolymerization of acrylonitrile (AN) and 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) by water phase precipitation copolymerization (WPPCP) method with $K_2S_2O_8$–Na_2SO_3 as initiator and water as reaction medium, which is illustrated in Fig. 1. Furthermore, PAN-co-AMPS was used as membrane material to prepare charged blend membrane.

On the other hand, phenolphthalein poly(ether sulfone) (PES-C) is a relatively newly developed engineering thermoplastic [19]. With regard to its chemical structure, as can be seen in Fig. 2, PES-C can be taken as poly(ether sulfone) modified by the introduction of the rather bulky and polarizable phenolphthalein group in place of oxygen atom. Due to its high performance and high stability, it has been sulfonated and then was used as membranes for gas permeation [20], ultrafiltration or nanofiltration [21], and fuel cell [22]. However, to our knowledge, few research results on membranes prepared directly by PES-C were reported. In view of its excellent mechanical and thermal properties, PES-C was selected as membrane materials in this study.

In a word, the objective of the present paper is to prepare blend membranes based on PES-C and PAN-co-AMPS with different composition and to investigate the hydrophilicity, electrical properties, water flux, retention and structure of the blend ultrafiltration membranes. The results of the investigation will be discussed in terms of the effect of polymer blend composition. In addition, the characteristics of PES-C/PAN-co-AMPS blend membranes have also been compared with pure PES-C membranes.

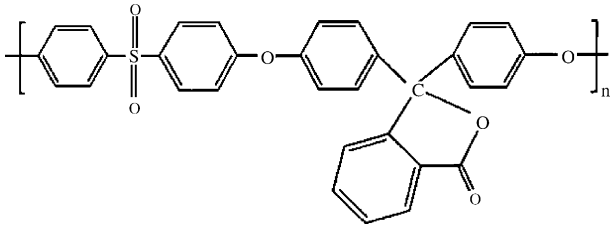

Fig. 2. The chemical structure of phenolphthalein poly(ether sulfone) (PES-C).

2. Experimental

2.1. Materials

Phenolphthalein poly(ether sulfone) used was supplied by Xuzhou Engineering Plastics Co., Xuzhou, China. Acrylonitrile was commercial product and was purified by vacuum distillation before used. Potassium persulfate ($K_2S_2O_8$) and anhydrous sodium sulfite (Na_2SO_3) were recrystallized by usual procedures. 2-Acrylamido-2-methylpropane-sulfonic acid was purchased from Aldrich and used as received without purification. In addition, DMF, KCl, HCl, KOH, and H_2SO_4 were all used directly without further purification.

2.2. Synthesis and characterization of PAN-co-AMPS

AN and AMPS were dissolved in deionized water and then added into a four-necked round flask equipped with mechanical stirrer, thermometer, and nitrogen inlet tube. Then, the pH of reaction mixture was adjusted appropriately by adding several drops of H_2SO_4. After the reaction vessel was purged with nitrogen for a while to remove all of dissolved oxygen, some amounts of $K_2S_2O_8$ and Na_2SO_3 were added into the stirring solution while maintaining the appropriate reaction temperature. The copolymerization was continued for a designed period of time, and the precipitated copolymer was filtered and washed with deionized water several times. At last, the obtained copolymer was dried under vacuum at 50 °C for 72 h.

IR spectra were measured on IR200 spectrometer purchased from Thermo Nicolet. The composition of the copolymer was determined by element analysis (Flash EA1112, Thermo Finnigan). Viscosity measurements were made in a thermostatic water bath at 25 ± 0.1 °C using a Ubbelohde viscometer. Copolymer was dissolved in DMF containing different amount of LiBr (from 0 to 0.1 M) and the viscosity of five concentrations was measured under each specified salt concentration. When the linear relation between the reduced viscosity (η_{sp}/C) and concentration (C) can be founded, the intrinsic viscosity was obtained by extrapolation of a plot of specific viscosity/concentration to infinite dilution using linear least squares.

2.3. Preparation of membrane

The ultrafiltration membranes were prepared by the classical phase inversion technique in water as coagulant. The compositions of the casting solution, its corresponding viscosity data