Materials Science and Engineering C 37 (2014) 68–75

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

A simple method to prepare modified polyethersulfone membrane with improved hydrophilic surface by one-pot: The effect of hydrophobic segment length and molecular weight of copolymers

Fen Ran [a,b,*], Jie Li [b], Yi Lu [a], Lingren Wang [a], Shengqiang Nie [a], Haiming Song [b], Lei Zhao [b], Shudong Sun [a], Changsheng Zhao [a,**]

[a] College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China
[b] School of Material Science and Engineering, State Key Laboratory of Gansu Advanced Non-Ferrous Metal Materials, Lanzhou University of Technology, Lanzhou 730050, People's Republic of China

ARTICLE INFO

Article history:
Received 13 February 2013
Received in revised form 3 December 2013
Accepted 27 December 2013
Available online 3 January 2014

Keywords:
Polyethersulfone membrane
One-pot
Amphiphilic triblock copolymer
Blood compatibility

ABSTRACT

A simple method to prepare modified polyethersulfone (PES) membrane by one-pot is provided, and the method includes three steps: polymerization of vinyl pyrrolidone (VP), copolymerization of methyl methacrylate (MMA) and blending with PES. The effect of the PMMA segment length and molecular weight of the copolymer (PVP-*b*-PMMA-*b*-PVP, as an additive) on the structures and properties of the modified membranes was investigated. Activated partial thromboplastin time (APTT) tests indicated that with the increase of the poly(methyl methacrylate) (PMMA) segment length in the chains of the copolymers and with the increase of the molecular weight of the copolymers, the APTTs of the modified membranes increased to some extent, since less of the additives were lost during liquid–liquid phase separation process. Therefore, the copolymer was designed and prepared with appropriate ratio of poly(vinyl pyrrolidone) (PVP) to MMA and with appropriate molecular weight for better membrane performance. When the copolymer was blended in the membrane, the water permeance, protein anti-fouling property and sieving coefficients for PEG-12000 increased obviously. The simple, credible and feasible method had the potential to be used for the modification of membranes with improved blood compatibility, ultrafiltration and antifouling properties of biomaterials and for practical production.

1. Introduction

Among the materials used in biomedical fields, polyethersulfone (PES) is one of the most important polymeric materials and is widely used in blood purification fields. PES and PES-based membranes show outstanding oxidative, thermal and hydrolytic stability as well as good mechanical and film-forming properties [1]. The membranes also show high permeability of middle molecular weight protein (such as Beta-microglobulin) when used as hemodialysis membranes [2]. However, injections of anticoagulants are needed when the membranes are used in hemodialysis [3]. To reduce the use of anticoagulants and further improve the blood compatibility of the biomaterials, many studies have focused on the development of new materials and the modification of conventional materials. The modification approaches mostly used for PES membranes include blending, coating, surface physical treatment, and surface grafting, etc [4–9]. Grafting antithrombogenic materials and/or hydrophilic polymers onto membrane material surfaces using chemical modification is an efficient method, while blending is the simplest method to modify PES membranes both for flat-sheet and hollow fiber membranes, and thus is widely used in industry [10].

By blending or grafting hydrophilic polymers onto PES membrane surfaces, such as poly(vinyl pyrrolidone) (PVP) [11], polyethyleneglycol (PEG) [12] and poly (acrylic acid-*co*-vinyl pyrrolidone) (PAA-*co*-PVP) [13,14] the surface hydrophilicity increased, the antifouling property and blood compatibility were also improved [15]. However, these hydrophilic polymers were water soluble, and the elution of the blended polymers from the PES membranes was unavoidable [16]. To avoid the elution, amphiphilic copolymers containing vinyl pyrrolidone (VP) chains were prepared in the recent studies [17,18]. A novel hydrophilic additive of silica-PVP nanocomposite was synthesized [19], and used to improve the surface coverage of PVP on the PES membrane surfaces for enhancing the antifouling property. The results indicated that the antifouling ability of the PES membrane with a silica-PVP nanocomposite additive was better than that with a PVP additive. Terpolymers of poly (acrylonitrile-*co*-acrylic acid-*co*-vinyl pyrrolidone) P(AN-*co*-AA-*co*-VP) [17] and poly (methyl methacrylate-*co*-acrylic acid-*co*-vinyl

* Correspondence to: F. Ran, School of Material Science and Engineering, State Key Laboratory of Gansu Advanced Non-Ferrous Metal Materials, Lanzhou University of Technology, Lanzhou 730050, People's Republic of China.
** Correspondence to: C.S. Zhao, College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China.
E-mail addresses: ranfen@163.com (F. Ran), zhaochsh70@163.com (C. Zhao).

0928-4931/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2013.12.037

pyrrolidone) P(MMA-*co*-AA-*co*-VP) [18] were used to blend with PES to prepare modified membranes. The terpolymers were water insoluble due to the AN (or MMA) chains. The terpolymers can be directly blended with PES as macromolecule additives using *N*-methyl-2-pyrrolidone (NMP) as the solvent to prepare membranes. When the terpolymers were blended in the membranes, protein adsorption decreased, while protein anti-fouling property increased. Furthermore, these amphiphilic copolymers have various molecular structures, such as linear [20], comb-like [21], dumbbell-like [22] and chain-sphere-like [23], and were used as additives to prepare blending membranes. However, few of the studies involved hemocompatibility, but focused on just anti-fouling property. In our recent study, an amphiphilic triblock copolymer of poly(vinyl pyrrolidone)-b-poly(methyl methacrylate)-b-poly(vinyl pyrrolidone) (PVP-b-PMMA-b-PVP) was synthesized and blended with PES to prepare membranes. The fact that PVP brush formed on the surface of the blended membrane endowed the membrane with good hydrophilicity. The modified membrane showed good blood compatibility, such as lowered protein adsorption, suppressed platelet adhesion and prolonged blood coagulation time, cytocompatibility, ultrafiltration and protein anti-fouling properties [24]. The above modification methods could effectively improve many properties of the PES membrane, the applications of these methods, however, have been largely limited because of the problems in the preparation process, such as long period, complex operation and many steps.

In this paper, a simple approach to modify PES membrane by one-pot method was provided. Compared with the stepwise synthesis method to prepare modified membranes by amphiphilic copolymers, which involves polymerization, copolymerization and blending, respectively; the simple method to prepare modified PES membranes with improved hydrophilic surface by one-pot was more simple, credible and feasible which may be applied to practical production. In addition, in order to find the optimal preparation condition and optimize the performance of the modified PES membrane, the effect of the PMMA segment length and molecular weight of the copolymer on the structures and properties of modified membranes was investigated in detail. The PVP chain brush formed on the surface of the membrane prepared endowed the membrane with good hydrophilicity. The blood clotting time, water permeance, protein anti-fouling property, and sieving coefficients for PEG-12000 of the modified PES membranes increased obviously.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Ultrason E6020P) was obtained from BASF, Germany. Methyl methacrylate (MMA; 99.0%) was purchased from UNI-CHEM, China. *N*-vinyl pyrrolidone (VP; 99.0%) was purchased from Alfa Aesar, USA, and was pretreated by activated carbons before use. *N, N*-dimethylacetamide (DMAC; AR, 99.0%) and *N, N*-dimethylformamide (DMF; 99.0%) were purchased from Chengdu Kelong Inc. (Chengdu, China) and used as the solvents. Azo-bis-isobutryonitrile (AIBN) was purchased from Chengdu Kelong Inc. (Chengdu, China) and used as the initiator. S,S′-bis(R,R′-dimethylacetic acid) trithiocarbonate (reversible addition-fragmentation chain transfer agent, RAFT agent) was prepared according to the literature [25]. All the other chemicals (analytical grade) were obtained from Chengdu Kelong Inc., China, and were used without further purification.

2.2. Preparation of the modified PES membrane

The copolymer modified PES membranes were prepared by one-pot method. The general procedure is as follows. VP, RAFT agent and AIBN were dissolved in DMF and deoxygenated by nitrogen gas for 30 min. After reacting at 80 °C for 4 h, MMA, AIBN and DMF were added. After reacting at 85 °C for another 12 h, the solutions were quenched in ice water to stop the polymerization. Then, PES was added with a certain volume of DMAC by vigorous stirring until clear homogeneous solution was obtained. After vacuum degassing, the casting solutions were prepared into flat sheet membranes by spin coating coupled with a liquid–liquid phase separation technique at room temperature [26]. The spin coating conditions were: rotation speed (1000–1500 rpm), rotation time (12–18 s) and at room temperature, and water was the non-solvent. The prepared membrane has a uniform thickness of about 50–80 μm, and a glass slide was used as substrate. The spin-coated membrane separated from the substrate automatically and easily when they were immersed in distilled water.

The concentration of PES was 16 wt.% and the contents of the copolymer in the casting solutions were 0, 3, 5 and 7 wt.%, respectively. The prepared membranes were put in distilled water for several days to remove the solvent (DMAC) and the physically adhered copolymer of PVP-b-PMMA-b-PVP.

The PMMA segment length and molecular weight of the copolymers could be modulated by controlling the VP/MMA/RAFT agent feed ratios. The prepared copolymers with the VP/MMA/RAFT agent feed ratios of 3.5/2.5/0.008, 3.5/1.2/0.016, 3.5/2.5/0.016, 3.5/5/0.016 and 3.5/2.5/0.035 (wt.) were termed A1, A2, A3, A4 and A5, respectively. The prepared PES membranes modified by A1, A2, A3, A4 and A5 were termed FSM-A1, FSM-A2, FSM-A3, FSM-A4 and FSM-A5, respectively.

2.3. Characterization

FTIR spectra of the copolymers were measured with FT-IR Nicolet560 (Nicol U.S.) instrument. To prepare FTIR samples, the polymers were dissolved in DMF and cast on a potassium bromide (KBr) disk with the thickness of about 0.8 mm. The ^{1}H NMR spectra were recorded on a Varian Unity Plus 300/54 NMR spectrometer using DMSO-*d* as the solvent at room temperature.

The morphologies of the membranes were observed by scanning electron microscopy (SEM) using an XL 30ESME scanning microscope. The membranes were firstly frozen in liquid nitrogen for several minutes and then broken. The membrane surfaces were also investigated by reflected FTIR and X-ray photoelectron spectroscopy (XPS). The hydrophilicity of the membrane surface was characterized on the basis of contact angle measurement using a contact angle goniometer (OCA20, Dataphysics, Germany) equipped with video capture. A piece of 2 cm × 2 cm membrane was attached on a glass slide and mounted on the goniometer. For the static contact angle measurements, a total of 3 μL double distilled water was dropped on the airside surface of the membrane at room temperature, and the contact angle was measured after 10 s. At least eight measurements were averaged to get a reliable value. The measurement error was ±3°.

2.4. Clotting time

To evaluate the antithrombogenicity of the membranes, activated partial thromboplastin time (APTT) was measured by an automated blood coagulation analyzer CA-50 (Sysmex Corporation, Kobe, Japan), and the test method was described in our previous paper [27]. Healthy human fresh blood (healthy, man, Chinese, 33 years old) was collected in vacuum tubes containing sodium citrate as an anticoagulant (anticoagulant to blood ratio, 1:9, *V/V*), and platelet-poor plasma (PPP) was obtained after centrifuging at 4000 rpm for 15 min.

2.5. Ultrafiltration of protein solution

Ultrafiltration of bovine serum albumin (BSA) solution was carried out to study the antifouling property of the modified PES membranes. Steady water permeance of the prepared membrane was measured using the apparatus as described in our previous studies [28,29]. The