



Preparation and characterization of sulfonated polyethersulfone membranes by a facile approach

Weifeng Zhao, Quanbing Mou, Xiaoxue Zhang, Jingyu Shi, Shudong Sun, Changsheng Zhao*

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

ARTICLE INFO

Article history:

Received 28 May 2012

Received in revised form 6 November 2012

Accepted 28 November 2012

Available online 19 December 2012

Keywords:

Sulfonated polyethersulfone

Hydrophilicity

Anticoagulant activity

Polyethersulfone membrane

ABSTRACT

Sulfonated polyethersulfone (SPES) was synthesized through a feasible way by introducing sulfonic groups onto amino-substituted PES, and characterized by FT-IR, ^1H NMR and GPC. The obtained SPES could be directly blended with PES at any ratios to prepare modified membranes. Scanning electron microscope indicated that the structure of the PES membranes had an obvious change after the modification. The water contact angles of the modified PES membranes decreased from 84° to 68° , and the water fluxes had a dramatic increase from 162 to 1912 mL/m² mmHg h when the blended amount of SPES increased from 0 to 2 wt.%. The activated partial thromboplastin time and plasma recalcification time for the modified membranes increased significantly, and the blood platelet adhesion on the PES membrane was largely suppressed after the modification. All these results indicated that the hydrophilicity and the anticoagulant activity of the modified PES membranes were improved, and the modified membranes had a potential to be used in blood purification fields.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Polyethersulfone (PES) is a favorable polymer for manufacturing membranes due to its excellent thermal tolerance, chemical stability, oxidation resistance, as well as good mechanical and film-forming characteristics [1]. PES and PES-based membranes have been widely used in advanced separation technology and biomedical fields such as artificial organs and medical devices used for blood purification [2–4]. However, the application of the PES membranes sometimes is limited by their hydrophobic nature, which led to membrane fouling due to the adsorption of nonpolar solutes, hydrophobic particles, or bacteria [5]. The adsorption behaviors often cause severe flux decline, substantial energy consumption and significant operational cost. With respect to improving the membrane properties, modifications of PES matrix have been addressed in several previous efforts; such modifications

could be achieved by supplying single group or multi-functional groups on the matrix and membrane surface, such as sulfonic ($-\text{SO}_3\text{H}$), hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), amino ($-\text{NH}_2$) groups and PEO macromolecules, or by combinations of them [6–11].

Among the functional PES membranes, sulfonated PES membranes had drawn great attention from scientists due to their wide applications for a variety of separation processes, such as reverse osmosis, ultra-filtration, ion exchange, and electro-dialysis processes and so on [11–13]. Since sulfonation is an aromatic electrophilic substitution reaction, the electro-donating substituents favor the reaction whereas electron-withdrawing groups do not. Therefore, PES is notoriously difficult to be sulfonated due to the electron withdrawing effect of the sulfone linkages which deactivate the adjacent aromatic rings for electrophilic substitution [14]. Of course, the sulfonation of PES can be conducted in homogeneous [15,16] and heterogeneous [17–20] media with different sulfonating agents and solvents. For homogeneous media system, Bikson et al. [15] conducted PES in concentrated chlorosulfonic acid, in the course of chlorosulfonation the aromatic rings

* Corresponding author. Tel.: +86 28 85400453; fax: +86 28 85405402.

E-mail addresses: zhaochsh70@scu.edu.cn, zhaochsh70@163.com (C. Zhao).

Nomenclature

| | | | |
|--------|---|------|---|
| Symbol | Meaning (common units) | WCA | The water contact angle of the membrane (°) |
| V | The volume of the permeated solution (mL) | APTT | The activated partial thromboplastin time of the membrane (sec) |
| S | The effective membrane area (m ²) | PRT | The plasma recalcification time of the membrane (sec) |
| t | The time of the solution collecting (h) | | |
| P | The pressure applied to the membrane (mmHg) | | |

of the polymer chain were substituted with chlorosulfonyl ($-\text{SO}_2\text{Cl}$) radicals and hydroxysulfonyl radicals ($-\text{SO}_3\text{H}$). Sulfonation of aromatic polyethersulfone could also be carried out using sulfur trioxide (SO_3) in concentrated sulfuric acid as solvent [16], and the resultant products were suitable for preparation of membranes. On the contrary, sulfonated polyarylethersulfones were derived by heterogeneous sulfonation of polymer/solvent intercrystallites of difficultly sulfonatable polyarylethersulfones in chlorinated hydrocarbon solvents with a sulfonation agent [17], the similar sulfonated system had also been conducted in another study [18]. PES could also be sulfonated by heterogeneous method using chlorosulfonic acid and methylene chloride as the solvent [19], SO_3 -triethylphosphate (TEP)/ CH_2Cl_2 was also used as sulfonating agents to prepare sulfonated PES membranes [20]. Although the post-sulfonation (those methods mentioned above) can introduce $-\text{SO}_3\text{H}$ into PES chain and be widely used due to its simplicity and low cost, the side reactions and degradation reactions are unavoidable.

Compared with post-sulfonation of PES materials, the pre-sulfonation starting from modified monomers possesses a pathway to control the molecular structure. Sampnerri et al. [21] prepared sulfonated copolyethersulfones using sulfonated monomers and previously synthesized telechelic hydroxy-ended poly (ether sulfone)s. Kim et al. [22] reported a cross-linked network structure of sulfonated poly(ether sulfone)s (PESs) with high proton conductivity, oxidative and hydrolytic stability, and low methanol diffusion coefficient. However, these pre-sulfonated PES materials were incapable of introducing other functional groups, which limited the application of the PES-based amphiphilic copolymers [23]. Fortunately, Zhu et al. [9] showed a readily modified PES with amino-substituted groups, several hydrophilic monomers such as *N*-isopropyl acrylamino (NIPAAm) and *N,N*-dimethylamino-2-ethyl methacrylate (DMAEMA) were successfully introduced into PES using the amino-substituted groups. In addition, Morita et al. [24] reported that the reaction of amino-substituted groups against SO_3 -pyridine complex could be easily conducted in DMF solvent. Therefore, the combination of the previous amino-substituted groups and post-sulfonated reaction will be a facile and powerful method to prepare sulfonated PES membranes. The advantage of the method was the possibility to control the substitution degree of the polymer by the structure of the feed monomer, and the avoidance of the side reactions and the degradation reactions during the post-sulfonation of PES.

The amino-substituted PES was synthesized via a condensation polymerization [9], and the amino groups

introduced to the polymer will endow PES with potential of facile modification via the post-functional method. The synthesized amino-substituted PES and the sulfonated PES polymers were investigated by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FT-IR). Then, the synthesized polymers were tested as additives to improve the hydrophilicity and the blood compatibility of the PES membranes. The contact angle, water flux, and the morphology and composition of the modified membranes were studied. Furthermore, the blood compatibility of the membranes including activated partial thromboplastin time (APTT), plasma recalcification time (PRT) and blood platelet adhesion, was also investigated.

2. Experimental section

2.1. Materials

Bis(3-amino-4-hydroxyphenyl) sulfone ($\geq 99\%$), bis(4-fluorophenyl) sulfone ($\geq 99\%$) and bis(4-hydroxyphenyl) sulfone ($\geq 99\%$) were supplied by Xiya reagent corporation and used without purification. *N,N*-Dimethyl acetamino (DMAc), toluene and other solvents (Chemical Reagent Factory of Kelong, China) were dried by stirring with CaH_2 and then distilled. Polyethersulfone (PES, Ultrason E6020P) was purchased from BASF, Germany and dried at 90°C for 24 h before use. All the other chemicals (analytical grade) were obtained from the Chemical Reagent Factory of Kelong, China, and were used without further purification.

2.2. Synthesis of SPES

In a representative procedure, bis(4-fluorophenyl) sulfone (5.08 g, 20.0 mmol), bis(3-amino-4-hydroxyphenyl) sulfone (2.24 g, 8.0 mmol), bis(4-hydroxyphenyl) sulfone (3.05 g, 12.0 mmol), DMAc (100 mL), toluene (80 mL) and potassium carbonate (K_2CO_3) were introduced to a three-neck round bottom flask equipped with a Dean–Stark device. After vacuuming and back-filling nitrogen for several times, the flask was transferred to the oil bath preheated to 145°C , and last for 4.5 h at nitrogen atmosphere. Then, the reaction system was heated to 180°C and last for 18 h. K_2CO_3 was used as proton scavenger, and the water formed during the reaction was removed as an azeotrope with toluene by the Dean–Stark device. The reaction mixture was cooled to room temperature and precipitated into ether. After volatilization of the ether, the residual monomers and K_2CO_3 in the product were removed by dispersing

Download English Version:

<https://daneshyari.com/en/article/10608831>

Download Persian Version:

<https://daneshyari.com/article/10608831>

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