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Polysulfone-based amphiphilic polymer for hydrophilicity and fouling-resistant modification of polyethersulfone membranes

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ABSTRACT

Polysulfone-based amphiphilic polymer polysulfone-*graft*-poly (ethylene glycol) methyl ether methacrylate (PSf-*g*-POEM) was synthesized and used to blend with polyethersulfone (PES) to tune the hydrophobicity and fouling-liable properties of PES membranes. Differential scanning calorimetry (DSC), contact angle measurements, X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM) were conducted to characterize the properties of blend membranes. DSC results showed that the blend samples were characterized with single T_g transition, indicating that the additives were compatible well with PES in membranes. Membranes hydrophilicity was evaluated by contact angle measurement and obviously enhanced wettability of blend membranes was found. XPS analysis suggested that poly (ethylene glycol) methyl ether methacrylate (POEM) brushes from amphiphilic additives occupied half part of the membrane surface composition, and the high content of POEM in surface had effectively improved the membranes hydrophilicity as well as the fouling-resistance to proteins. Meanwhile, the formation of cake layer was explored as a main reason for membrane fouling behavior, while the irreversible filtration resistance (R_{ir}) could be greatly reduced by incorporation of the synthesized amphiphilic additives. SEM was also conducted to inspect the morphologies of blend membranes.

1. Introduction

Polyethersulfone (PES) is a favorable membrane material due to its good membrane-forming and excellent physicochemical properties, and the usage are widely found from water treatment to biological dialysis [1–9]. However, the intrinsic hydrophobicity of PES always makes the membrane preferentially interact with the natural organic material (NOM) like humic substance or biomolecules in the feed solutions [2,3,10], and it becomes fouled. These fouling phenomena can be evidenced by flux-decreasing and expressed as the increasing of the filtration resistance.

Hydrophilicity modification is helpful to reduce the membrane fouling and prevent the flux-decreasing. In the works about membranes hydrophilic modification, blending [11], coating [12], surface grafting [13], surface physical treatment [14] and physical adsorption [15] are found. Compared to the other methods, blending with amphiphilic copolymer shows the advantage of permanent modification efficiency as well as the facile manipulation [16], and it is commonly adopted. However, only several examples are found for PES membranes hydrophilic modification using its amphiphilic polymers, which perhaps because the highly stable structure of PES and the difficult availability of PES-based amphiphilic additives [17]. Although several methods have been implemented to endow PES with hydrophilicity, either conducting PES in concentrated H_2SO_4 [18] or in chlorosulfonic acid [19,20], and limitations were found for both reactions from two sides that: firstly, the extreme solvents always caused the degradation and mechanical performance deterioration for PES material; secondly, they were incapable of introducing functional groups that were used to initiate radical polymerization of various monomers, which seems to be the main reason why the PES-based amphiphilic copolymers are limited to a few kinds. Compared to PES, PSf is much easier to be modified though they are both aromatic polysulfones, and PSf-based ATRP macroinitiator can be facilely synthesized by nucleophilic substitution of chloromethylate group in bisphenol unit [21]. As a result, various water soluble monomers such as poly (ethylene glycol) methyl ether methacrylate (POEM) and hydroxyethylene methacrylate (HEMA) can be grafted to PSf, and the PSf-based amphiphilic copolymers will be conveniently synthesized. On the other hand, since it is not easy for PES modification, foreign copolymers like MPC [22], PAI [23], F127 [24,25] and others [26] which are not PES-based were also explored to blend with PES. This probably means that the PES membranes modification needs not be limited to PES-based amphiphilic polymers, and the materials that share good compatibility with PES are all suitable candidates. From this consideration, the PSf-based amphiphilic

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polymers are potential candidates because of the structure similarity and possible compatibility, at the same time, the use of PSf-based copolymer to modify PES membranes has not been found.

In present work, we first synthesized amphiphilic polysulfone-*graft*-poly (ethylene glycol) methyl ether methacrylate (PSf-*g*-POEM) through atom transfer radical polymerization (ATRP) and then used it as a modifier to PES membranes. Water contact angle measurement and X-rays photoelectron spectroscopy were conducted to analyze the surface properties of blend membranes. Filtration resistances including irreversible fouling-resistance (R_{ir}) and cake layer resistance (R_c) were determined to get insight into PES membranes fouling process. Finally, membranes morphologies of membranes were observed by scanning electron microscope (SEM).

2. Experimental

2.1. Materials and reagents

Polyethersulfone (PES, RADEL A100, M_w = 53,500 g/mol) and Polysulfone (PSf Udel P3500LCD, M_w = 26,000 g/mol) were both purchased from Solvay Advanced Polymers. Poly (ethylene glycol) methyl ether methacrylate (POEM, 97%, Mn 475 g/mol) was obtained from Aldrich Chemical Co. (Milwaukee, WI). It was passed through an inhibitor removing column with aluminium oxide before using. Copper(I) chloride (CuCl, ≧99%) was supplied by Aldrich Chemical Co. and the purification method followed the earlier literature [27], bovine serum albumin (BSA, M_w 67,000) was supplied by Bio Life Science and Technology Co. (Shanghai, PR China),1-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc) and other reagents were all chemical purification and were used directly.

2.2. Synthesis of PSf-g-POEM by ATRP

Typically, the synthesis of PSf-g-POEM was conducted by first chloromethylation of PSf material following a procedure described elsewhere [21]. Subsequently, 5.0 g of PSf-CH_2Cl and a certain amount of POEM, $CuCl_2$ as well as 2,2-biphenyl (bpy) was dissolved into 50 ml NMP. After 30 min bubbling of nitrogen, CuCl was imported, and the polymerization was started by raising the temperature to 80 °C in an oil bath, and reaction was terminated after 24 h grafting. The weight percent of POEM in amphiphilic polymer was determined to 32.3 wt% by ^{1}H NMR and the spectrum was shown shown in Fig. 1. The assignment of the spectrum is completed by following the literature [21], and the grafting yield is obtained by calculating the relative intensity of the peak at 3.68 ppm to 7.9 ppm (I3.68/I7.9).

Table 1
Compositions of casting solution for PES and blend membranes.

ID	PES (g)	PSf-*g*-POEM (g)	PVP (g)	DMAc (g)
M1	20	0	5	75
M2	17	3	5	75
M3	16	4	5	75
M4	15	5	5	75

2.3. Membrane preparation

Membranes were prepared by classical immersion precipitation method in this work. Besides 5 wt% of PVP (K30) was used as pore former, another 20 wt% of polymers constituted with set ratios of PSf-*g*-POEM/PES were dissolved in DMAc. The compositions for the casting solution are shown in Table 1. After fully dissolving, the filtrated polymer solutions were casted onto the glass plate (~200 μm in thickness), and then immersed into a coagulation bath constituted with H_2O and DMAc by volume ratio of 40/60 for 5 min. Next, the gelled membranes were quenched in 90 °C water for 24 h, and the resulted membranes were washed with de-ionized water and air-dried for characterization.

2.4. Characterization

The contact angle of the membranes was surveyed on contact angle goniometer (OCA20, Dataphysics Instruments with GmbH, Germany) at 28 °C, 60% relative humidity. The reported data were averaged from more than seven determinations at differ-

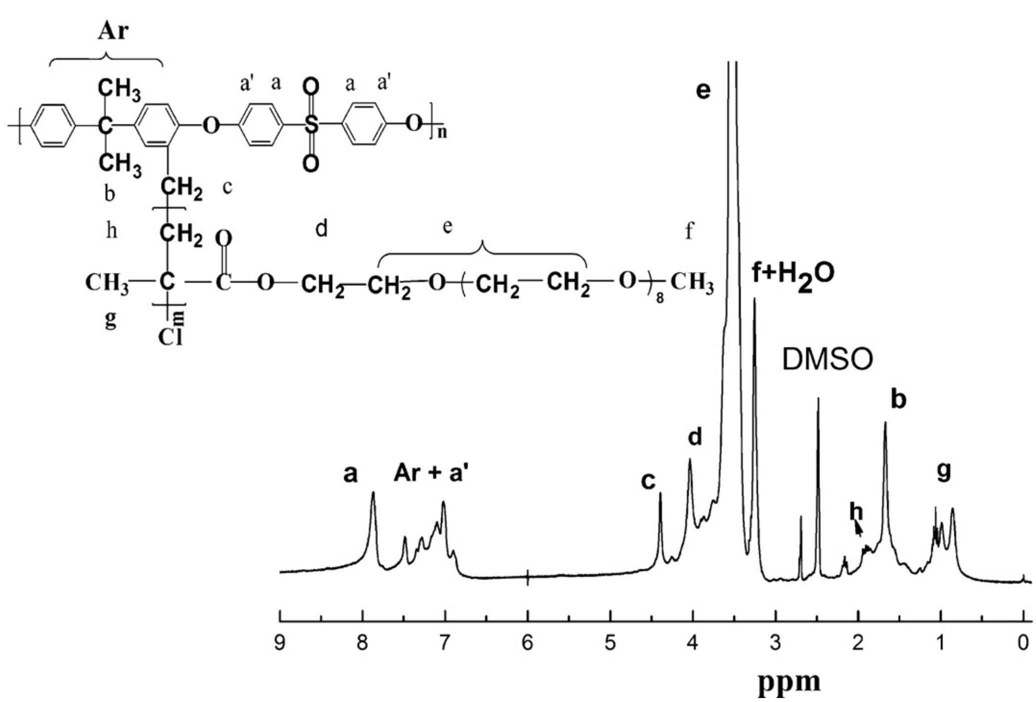

Fig. 1. NMR spectrum for the synthesized PSf-g-POEM.