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Synthesis and characterizations of novel, positively charged hybrid membranes from poly(2,6-dimethyl-1,4-phenylene oxide)

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Abstract

A series of PPO based organic–inorganic hybrid membranes with both strong and weak base groups were prepared though sol–gel process of 3-aminopropyl-trimethoxysilane (A1110) and polymer precursors PPO–Si$(OCH_3)_3$(+), which were obtained by reacting bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) with A1110 and trimethylamine (TMA). The chemical structure of the step reaction products was confirmed by FT-IR measurements. The final hybrid membranes were characterized by TGA, IEC, SEM, water flux, water uptake, rejection rate as well as streaming potential. Results showed that the prepared hybrid membranes possessed higher thermal stability than usual polymeric charged membranes, anion exchange capacity range (2.44–2.95 mmol/g dry membrane), low water flux (5.09–12.26 L/(m^2 bar h)), positively streaming potential even at high pH value, and decreasing water uptake and rejection rate towards gelatin when pH value increases.

Keywords: Organic–inorganic hybrid membranes; Positively charged membrane; Sol–gel; PPO

1. Introduction

Nanofiltration (NF) and ultrafiltration (UF) are two important pressure-driven processes and are widely used in industries [1,2]. Ultrafiltration membranes reject macromolecules but pass dissolved ions. However, nanofiltration membranes pass mono-valent to a certain extent, but they reject multivalent ions and low molecular weight molecules [1]. To separate or reject ions or reduce the fouling from the treated feed, these two kinds of membranes not only need proper pores structure, but also need charge on the surface. Unfortunately, driven by commercial interests, the negatively charged membranes used for antifouling in the separation of biochemical products have been deserved much attention in recent years [3], while the development of a positively charged membrane is ignored due to its seldom applications [4]. But to separate species with positive charge, such as the separation of biomacromolecules below the isoelectric point, and recover cathode electrophoresis lacquer, etc., positively charged membranes for NF or UF are actually needed. Especially, such applications often concern with severe conditions such as high temperature, strongly oxidizing conditions or organic solvents, under which organic charged membrane is limited in its characteristics.

Therefore, organic–inorganic hybrid materials have now been attracted great attention for preparing charged membranes because of their unique opportunity to combine the remarkable features of organic materials with those of inorganic materials [5–10]. For the preparation of this kind of materials, incorporation of inorganic network through sol–gel process into a polymer matrix is commonly employed [5,7]. High degree of homogeneity between the inorganic network and the polymer component can be achieved by introducing chemical bonds between the organic and inor-

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ganic phases. One route for forming such chemically bonded organic–inorganic hybrid materials is to utilize organic polymers functionalized with trialkoxysilane groups as the sol–gel precursors [5,11].

In our lab, we have utilized such route to prepare positively charged hybrid membranes: Polyethylene oxide (PEO)-400 was end-capped with silane containing secondary amine and trialkoxysilane groups. Through the sol–gel process of this obtained polymer precursor and quarteramination reaction afterwards, positively charged membranes were obtained [12]. We have also prepared a novel, positively charged poly(methyl acrylate) (PMA)–SiO_2 nanocomposite through the sol–gel process of positively charged alkoxysilane-containing polymer precursors, which were synthesized by coupling different amounts of *N*-[3-(trimethoxysilyl)propyl]ethylene diamine (A1120) to poly(methyl acrylate) (PMA), followed by a quaternization reaction [13]. The positively charged hybrid membranes or materials prepared in such way showed excellent properties in thermal stability and compatibility [12,13]. To find the variety in preparing positively charged hybrid membranes with higher thermal stability, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was chosen as the starting polymer with the two considerations: one is that PPO, characterized by a high glass transition temperature ($T_g = 212\,^\circ C$) and good thermal stability under nonoxidizing conditions, is one of the most widely used engineering plastics [14]; the other is that PPO has been successfully developed for a series of novel positively charged or anion exchange polymeric membranes in our lab by bromination and the subsequent amination [15–19]. Therefore, the current work will focus on introducing inorganic content to PPO by reacting bromomethylated PPO (BPPO) with 3-aminopropyl-trimethoxysilane (A1110) and trimethylamine (TMA). The obtained polymer precursors then underwent hydrolysis and condensation together with A1110 in the presence of aqueous HCl catalyst. The properties of the prepared positively charged hybrid membranes, such as thermal stability, IEC, streaming potential, water uptake, rejection rate and pure water flux, are reported and fully discussed in this article.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of intrinsic viscosity equal to 0.57 dL/g in chloroform at 25 °C was obtained from Institute of Chemical Engineering of Beijing (China); chlorobenzene, dimethyl formamide (DMF) and *n*-hexane were carefully dehydrated with molecule sieves before use. Trimethylamine (TMA) was purified from its saturated aqueous solution by heating and collected by dehydrated DMF. A1110 was of analytical grade and was used as received.

Asymmetrical microporous alumina plates, with a thin top Al_2O_3 layer (average pore size about 0.2–0.3 μm) and a support ceramic layer (average pore size about 1 μm), were commercially obtained from Institute for Ceramic Research in ZiBo (Shandong, China). Total thickness of the alumina plates was around 0.45 cm.

2.2. Preparation of the dipping solution

The poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was first bromomethylated according to the procedure described in our previous papers [16,17], and the benzyl substitution ratio is calculated to be 0.8 through ^1H NMR data of bromomethylated PPO (BPPO). In the mixture solution of chlorobenzene and dimethyl formamide (DMF) (volume ratio of chlorobenzene to DMF is 1:1), BPPO first reacted with trimethylamine (TMA) and A1110 under nitrogen atmosphere. In this reaction system, the molar ratio of BPPO and A1110 was kept to be 1, and the concentration of BPPO was 5% (w/v). As shown in Table 1, the weight ratio of TMA, η, which is defined as η = [weight of TMA]/[weight of A1110 + weight of BPPO + weight of TMA] ranges from 0.03 to 0.13. The mixture solution was stirred for 24 h, then part of it was taken out, precipitated and washed with *n*-hexane for several times to eliminate the unreacted A1110 and get the polymer precursor PPO–$Si(OCH_3)_3(+)$. Into the rest of the reaction mixture, HCl solution (0.001 mol/mol water) was added (H_2O:HCl:alkoxides = 1:0.001:1, molar

Table 1
Feed composition and the residue in TGA for both the polymer precursors and the prepared membranes

Membranes	Weight ratio of TMA, η[a] in feed composition	Residue of polymer precursors in TGA[b] (wt%)	Residue of the prepared membrane in TGA[b] (wt%)	x_{TGA}[c]	x_{IEC}[d]
A	0.13	13.00	19.72	0.68	0.68
B	0.07	14.80	20.99	0.79	0.76
C	0.05	16.62	21.78	0.89	0.80
D	0.03	18.47	22.54	1.00	0.85
Reference	0	21.03	23.87	1.22	–

[a] η = [weight of TMA]/[weight of A1110 + weight of BPPO + weight of TMA].

[b] Residual contents are obtained at 800 °C from TGA thermograms, which were performed at heating rate 10 °C/min under air atmosphere.

[c] x_{TGA} was calculated according to the residual content of polymer precursors assuming that all the $-Si(OCH_3)$ groups in the polymer precursors changed to silica and no other component remained at 800 °C.

[d] x_{IEC} was calculated from the IEC_s listed in Table 2.