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Journal of Membrane Science 315 (2008) 20–27

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Polyamide thin film composite membranes prepared from isomeric biphenyl tetraacyl chloride and *m*-phenylenediamine

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Received 5 October 2007; received in revised form 22 January 2008; accepted 1 February 2008
Available online 21 February 2008

Abstract

Three novel of isomeric tetra-functional biphenyl acid chloride: 3,3′,5,5′-biphenyl tetraacyl chloride (mm-BTEC), 2,2′,4,4′-biphenyl tetraacyl chloride (om-BTEC), and 2,2′,5,5′-biphenyl tetraacyl chloride (op-BTEC) were synthesized, and used as new monomers for the preparation of the thin film composite (TFC) reverse osmosis (RO) membranes through interfacial polymerization with *m*-phenylenediamine (MPDA). The results of membrane performance test showed that membranes prepared from om-BTEC and op-BTEC had higher flux at the expanse of rejection compared with membranes prepared from mm-BTEC. The chemical composition on the active layer was characterized by attenuated total reflectance infrared (ATR-IR) and X-ray photoelectronic spectroscopy (XPS), and the results showed that the content of carboxylic acid on the membrane surface prepared from mm-BTEC are higher than these prepared from op-BTEC and om-BTEC. It seemed that all the difference containing: the membrane performance, the chemical composition on the active layer, hydrophilicity, and the surface morphology might come from the different structure and reactivity of the tetraacyl chloride monomers.

Keywords: Reverse osmosis; Thin film composite; Polyamides; Selectivity

1. Introduction

Reverse osmosis separation has attracted significant research attention as an economic process in the field of water desalination, ultra-pure water production, and waste-water treatment [1]. Thin film composite (TFC) membranes fabricated via interfacial polymerization (IP) have been proved to be the most successful RO membranes. They typically consist of three structural components: (1) top ultra-thin skin polyamide layer; (2) middle polysulfone porous support; (3) bottom non-woven polyester fabric. In TFC membranes, the active skin layer is the key component, which controls mainly the separation properties of the membrane, while the support layer gives the membrane necessary mechanical properties. The materials used to produce the skin layer included polyamides from aliphatic or aromatic diamine [2–5], poly(aminostyrene) [6,7] and the cross-linkers such as trimesoyl chloride (TMC), isophthaloyl chloride and terephthaloyl chloride. Other polymers such as polyurea, polyurea-amide, polyether-amides etc. [8–13] had been investigated as candidate TFC materials. Among these polymers, the cross-linked aromatic polyamide which is produced by the interfacial polymerization of *m*-phenylenediamine (MPDA) and TMC is the most successful commercial product.

The TFC membrane performances of polyamides are influenced by several structural and processing variables, such as primary polymer structure (*m*/*p*-phenylene units), casting solution composition, evaporation period, post-annealing treatments, etc. In terms of polymer structure, it was believed that several factors could influence the membrane performances, such as monomer size, solubility, shape and reactivity [14]. Over the past decades a body of knowledge had been developed which related polymer structure to its solute permeability and other physical properties. Mickols, for example patented the work on flux enhancement by varying the type of amine employed [15]. Roh had studied the effect of the isomeric

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doi:10.1016/j.memsci.2008.02.022

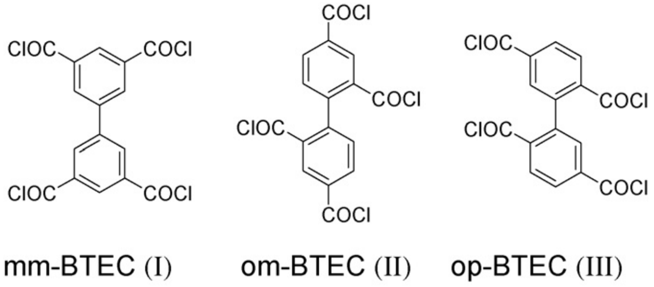

Fig. 1. Structures of the acyl chloride monomers.

diamine monomers on membrane performances [16]. It was revealed that the *meta*-positioned polyamide (TMC/MPDA) had higher hydrophilicity and greater molecular chain mobility than the *para*-positioned polyamide (TMC/PPDA), hence, resulting in higher water flux. Moreover, Kim et al. had studied how membrane performance was related to the molecular structure of aromatic polyamides and the incorporation of poly(*p*-aminostyrene) or poly(*m*-aminostyrene) to the aromatic polyamides for fabricating active skin layer affects the membrane performance [6,7].

Since the IP process is diffusion controlled in the organic layer [17], the effect of organic phase reactant is likely to have a great impact on membrane performance. In previous paper, we reported that the preparation of polyamide TFC membranes from 3,3′,5,5′-biphenyl tetraacyl chloride (**I**, mm-BTEC) and MPDA, and found that the membrane had lower flux and higher rejection compared with the membrane prepared from TMC/MPDA [18]. As a continuation of this study, the other two isomeric compounds: 2,2′,4,4′-biphenyl tetraacyl chloride (**II**, om-BTEC) and 2,2′,5,5′-biphenyl tetraacyl chloride (**III**, op-BTEC) were synthesized and used as the monomers for the preparation of polyamide TFC membranes (Fig. 1). In this paper, we reported the preparation of isomeric biphenyl tetraacyl chloride-based polyamide RO membranes. The relation between the acyl chloride monomer structure and the membrane performance, the chemical composition of the active layer, hydrophilicity, surface morphology were discussed in this paper.

2. Experimental

2.1. Synthesis of monomers

2.1.1. Materials

Reagent grade anhydrous $NiBr_2$ was dried at 250 °C under vacuum. Triphenylphosphine (PPh_3) was recrystallized from hexane. Powdered (100 mesh) zinc was stirred with acetic acid, filtrated, washed thoroughly with diethyl ether, and dried under vacuum. *N*,*N*-dimethylacetamide (DMAc) was stirred over phosphorous pentoxide for 5 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves. Copper powdered (shot 1–10 mm) was purchased from Acros. Other reagents and solvents were obtained commercially and used without further purification.

2.1.2. Synthesis of 2,2′,5,5′-tetramethyl-1,1′-biphenyl

The 2,2′,5,5′-tetramethyl-1,1′-biphenyl was prepared from 1-bromo-2,5-dimethylbenzene by following the literature procedure [19]. ^1H NMR ($CDCl_3$, ppm): δ 7.145–7.120 (d, 2H), 7.065–7.040 (d, 2H), 6.915 (s, 2H), 2.328 (s, 6H), 2.013 (s, 6H).

2.1.3. Synthesis of 2,2′,5,5′-biphenyl tetracarboxylic acid

The 2,2′,5,5′-biphenyl tetracarboxylic acid was prepared by following the literature procedure [20]. ^1H NMR (DMSO-d_6, ppm): δ8.00 (m, 4H), 7.68 (s, 2H).

2.1.4. Synthesis of 2,2′,5,5′-biphenyl tetraacyl chloride

The 2,2′,5,5′-biphenyl tetracarboxylic acid (3.3 g, 10 mmol) was reacted with $SOCl_2$ (7.3 ml, 100 mmol) for 8 h under reflux. After evaporation of $SOCl_2$, the residue was recrystallized from hexane to give the final product. ^1H NMR ($CDCl_3$, ppm): δ 8.459–8.431 (d, 2H), 8.371–8.343 (dd, 2H, $J = 1.5$ Hz), 7.943–7.938 (d, 2H, $J = 1.5$ Hz). IR (KBr, cm^{-1}): 1767, and 1743. Anal. Calcd. for $C_{16}O_4Cl_4H_6$: C, 47.52%, H, 1.49%, Cl, 35.15%. Found: C, 47.54%, H, 1.50%, Cl, 35.11%.

2.1.5. Synthesis of 2,2′,4,4′-biphenyl tetraacyl chloride

The 2,2′,4,4′-biphenyl tetraacyl chloride (om-BTEC) was prepared from 1,3-dimethyl-4-bromobenzene dicarboxylate following the literature [21]. ^1H NMR ($CDCl_3$, ppm): 8.987–8.981 (d, 2H, $J = 1.8$ Hz), 8.366–8.339 (dd, 2H, $J = 1.8$ Hz), 7.311–7.284 (d, 2H,). IR (KBr, cm^{-1}): 1765, and 1742. Anal. Calcd. for $C_{16}O_4Cl_4H_6$: C, 47.52%, H, 1.49%, Cl, 35.15%. Found: C, 47.50%, H, 1.48%, Cl, 35.17%.

2.2. Preparation of the composite membrane

2.2.1. Preparation of microporous polysulfone support membrane

To fabricate the TFC membrane, a support substrate composed of microporous polysulfone was first prepared by the following procedures. A solution of 16.5% (by weight) polysulfone (Udel P-3500, U.S. Amono Comp), 13.5% ethyleneglycol monomethyl ether (EGM), 0.03% dodecyl sulfonic acid sodium salt (DDS) and DMF 69.97% was cast onto a glass plate with a polyester non-woven fabric using a 0.29-mm knife gape. The plate was immediately immersed in a water bath at room temperature in one smooth motion. Within 30 s the PS gelled into a white microporous sheet, and the top face was used as a support surface for the TFC membrane.

2.2.2. Fabrication of thin film composite membrane

The active skin layer of the composite membrane was prepared by interfacial polymerization technology. First, the aqueous solution containing MPDA (2%, w/v), triethyl amine (TEA) (1%) and dodecyl sulfonic acid sodium salt (DSS) (0.05%, w/v) was prepared with pH 10 adjusted by camphor sulfonic acid. Then, the aqueous solution was poured on top of the support membrane and allowed to soak in 3 min. Excess solution was drained from the dip-coated surface and air-dried at room temperature until no remaining liquids. Afterwards, the organic