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Aromatic-cycloaliphatic polyamide thin-film composite membrane with improved chlorine resistance prepared from *m*-phenylenediamine-4-methyl and cyclohexane-1,3,5-tricarbonyl chloride

Sanchuan Yu[a,*], Meihong Liu[a], Zhenhua Lü[a], Yong Zhou[b], Congjie Gao[b]

[a] *Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Education Ministry, Zhejiang Sci-Tech University, Hangzhou 310018, PR China*
[b] *The Development Center of Water Treatment Technology, SOA, Hangzhou 310012, PR China*

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ABSTRACT

Aromatic-cycloaliphatic polyamide thin-film composite (TFC) reverse osmosis (RO) membranes with improved chlorine resistance as well as good RO performance were developed by the interfacial polymerization of *m*-phenylenediamine-4-methyl (MMPD) and cyclohexane-1,3,5-tricarbonyl chloride (HTC) on polysulfone supporting film. Parametric studies were carried out to optimize the performance of the TFC membrane. The RO performance including salt rejection and water flux of the resultant membrane was evaluated through permeation experiment, the properties of TFC membrane were characterized by AFM, SEM, XPS, ATR-IR and contact angle measurement, and the chlorine resistance was studied by measuring the chlorine uptake rate of the polyamide and the evaluation of membrane performance before and after hypochlorite exposure. The results reveal that the TFC membrane prepared from MMPD and HTC exhibits higher chlorine resistance and better-matched water flux compared with that prepared from *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) at the expense of some salt rejection. The desired membrane prepared under the optimum condition exhibits a typical salt rejection of 97.5% and a water flux of 53.0 l/m^2 h for brackish water desalination, and an attractive chlorine resistance of more than 3000 ppmh Cl. The high chlorine resistance is attributed to the reduced probability of N-chlorination and Orton-rearrangement by using monomer MMPD.

1. Introduction

Reverse osmosis separation technology has attracted significant research attention as an economic process in the field of water desalination, ultra-pure water production, and wastewater treatment [1]. The concept of reverse osmosis (RO) treatment was started through the development of the asymmetric cellulose acetate membrane by Loeb and Sourirajan in the 1960s [2]. The major breakthrough in this field was achieved with the development of thin-film-composite (TFC) membrane with high flux and selectivity by the interfacial polymerization [3–5], which brought about the current worldwide expansion and diverse applications of the RO membrane in commercial water treatment and water pollution control. 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. Composite membranes have advantages over single-material asymmetric membranes in that, the top-active layer is formed in situ and hence the chemistry and performance of the top barrier layer and the bottom porous substrate can be independently modified to maximize the overall membrane performance. The materials are used to produce the skin layer, including polyamides from aliphatic or aromatic diamine [6–9] and the cross-linkers, such as trimesoyl chloride (TMC), isophthaloyl chloride and terephthaloyl chloride. Other polymers, such as polyurea, polyamide-urea, polyether-amides, polyamide-urethane [10–14] also have been investigated as candidate thin-film materials of TFC membrane. Among these polymers, aromatic polyamide produced through interfacial polymerization of an aromatic polyamine with one or more aromatic polyacyl chlorides is widely used in the thin-film polymers of TFC membrane in the commercial use.

The TFC membrane performances of polyamides are influenced by several structural and processing variables, such as primary polymer structure, casting solution composition, evaporation period, post-annealing treatment. In terms of polymer structure, several factors about the membrane performances are taken into consideration, such as monomer size, solubility, shape and reactivity [5]. Over the past decades much research has been done, which relates polymer structure to its solute permeability and other physical properties. Arthur [15], for example,

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* Corresponding author. Tel.: +86 571 86843217; fax: +86 571 86843217.
E-mail address: yuschn@163.com (S. Yu).

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studied the structure–property relationship in thin-film composite membranes prepared from different polyacyl chlorides. Trimesoyl chloride, cyclohexane-1,3,5-tricarbonyl chloride (HTC) and adamantane-2,6-dione-1,3,5,7-tetracarbonyl chloride (ADTC) were selected as the polyacyl chlorides to react interfacially with *m*-phenylenediamine to produce the thin skin layer. Both the HTC and ADTC analogs showed higher water flux than the TMC analog, but at lesser salt rejection levels. Roh [16] studied the effect of the isomeric diamine monomers on membrane performances. 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, the effect of the molecular structure of the thin-film polymer on the reverse osmosis performance was investigated by Kim et al. [17,18]. Various benzenediamines and poly(aminostyrene) were used to react interfacially with various acryl chlorides to produce the thin skin layer. The obtained membrane showed typical trade-off behavior between the salt rejection and water permeability. Membrane prepared from 1,3,5-benzenetricarbonyl trichloride (TMC) and a mixture of *m*-phenylenediamine and poly(aminostyrene) showed higher performance than usual membranes.

To date, the TFC membranes comprising aromatic polyamide thin film have reached a relatively high level in regard to the salt rejection and water permeability. However, it has been pointed out that aromatic polyamides are very sensitive to a chlorine disinfectant, which is commonly used in the field of seawater desalination and food processing. Few papers on the improvement of chlorine resistance are reported and thus this remains an important objective. Kawaguchi and Tamura [19] observed that reversible and irreversible chlorination occurred in polyamides upon chlorine exposure and these modes were dependent on the amine component of polyamide. Konagaya and Watanabe [20] prepared various polyamides from isophthaloyl dichloride and aliphatic, cycloaliphatic and aromatic diamines. The influence of the chemical structures of the polyamides on chlorine resistance was studied by measuring their chlorine uptake rates. The experiments indicated that the chlorine resistance of the polyamides could be effectively improved by using aromatic diamines compounds with a mono Cl or CH_3 substituent at the *ortho* position of the amino group. Moreover, Shintania et al. [21] investigated the chlorine resistance of polyamides synthesized using various diamines and acid chlorides. The results showed that the chlorine resistance generally increased in the order of polyamides synthesized from aromatic, cycloaliphatic and aliphatic diamines, respectively. The polyamides from diamine with amino groups at *ortho*-position showed better chlorine resistance, compared with those with amino groups at *meta*- and *para*-position. Secondary diamines were also useful to prepare the polyamide with high chlorine resistance.

In this article, we report the development of aromatic-cycloaliphatic polyamide thin-film composite reverse osmosis membrane with improved chlorine resistance as well as good RO performance. Thin-film composite reverse osmosis membranes were prepared through an interfacial polymerization technique on the polysulfone supporting film. The chemical structures of the monomers used in this study are shown in Fig. 1. Monomers *m*-phenylenediamine-4-methyl (MMPD) and cyclohexane-1,3,5-tricarbonyl chloride (HTC) were selected to prepare aromatic-cycloaliphatic polyamide thin-film composite membranes. It was believed that the aromatic diamine compound MMPD with a CH_3 substituent at the *ortho* position of the amino would produce the polyamide possessing an improved chlorine resistance, while the monomer HTC with some conformational mobility would produce the polyamide possessing an improved permeability. The fabrication of the TFC membranes on a polysulfone supporting film through interfacial polymerization with MMPD and HTC is reported in this article. The reverse osmosis performance, chlorine uptake and chemical structure of the polymer, hydrophilicity of the active layer, morphology of the TFC membrane, as well as the chlorine resistance and long-term performance stability of the resulting membrane are also discussed.

2. Experimental

2.1. Monomers

m-Phenylenediamine-4-methyl (MMPD; 2,4-diaminotoulene; purity > 99.5%) and *m*-phenylenediamine (MPD; purity > 99.5%) were purchased from Shanghai Amino-Chem. Co. Ltd., China. Trimesoyl chloride (TMC; purity > 99.0%) was purchased from Qin Dao Ocean Chem. Co., China. Cyclohexane-1,3,5-tricarbonyl chloride (HTC) was synthesized via the method of Weyland and Hamel [22] from 1,3,5-cyclohexanetricarboxylic acid (HTA) as outlined in Scheme 1. The 1,3,5-cyclohexanetricarboxylic acid (HTA) was prepared via catalytic hydrogenation of trimesic acid by following the literature procedure [23]. Yield: 90%, m.p.: 218–219 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 12.23 (s, 3H, COOH), δ 2.357 (t, 3H, O=C–CH), δ 2.09 (d, 3H, CH), δ 1.24 (t, 3H, CH). ^{13}C NMR (d_6-DMSO, ppm) δ 175.46, 40.58, 30.45. IR (KBr, cm^{-1}): 1699, 2975 and 3402. Anal. calcd. for $C_9O_6H_{12}$: C, 50.00%, H, 5.59%. Found: C, 50.61%, H, 5.75%. Then the 1,3,5-cyclohexanetricarboxylic acid (10.8 g, 0.05 mol) was reacted with thionyl chloride ($SOCl_2$) (23.8 g, 0.2 mol) for 12 h under reflux. After evaporation of $SOCl_2$, the residue was further distilled at 165 °C and 0.45 mmHg to give the final product of cyclohexane-1,3,5-tricarbonyl chloride (HTC). Yield: 75%. ^{1}H NMR ($CDCl_3$, ppm): δ 2.89 (m, 3H, O=C–CH), δ 2.68 (d, 3H, CH), δ 1.75 (q, 3H, CH). Anal. calcd. for $C_9O_3Cl_3H_9$: C, 39.78%, H, 3.31%, Cl, 39.22%. Found: C, 40.56%, H, 3.59%, Cl, 38.92%.

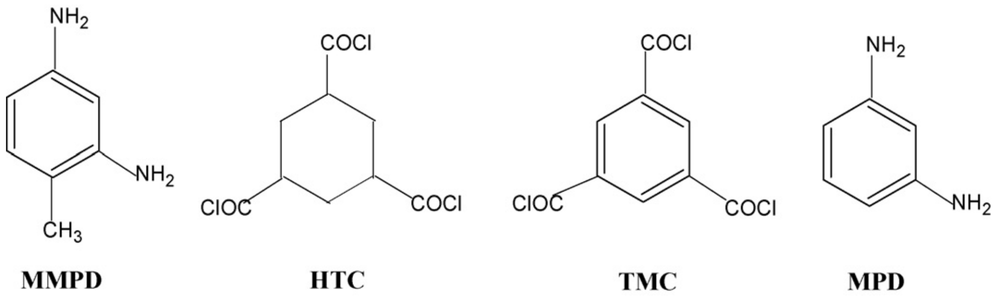

Fig. 1. Chemical structure of the monomers for preparation of TFC membranes (MMPD: *m*-phenylenediamine-4-methyl; HTC: cyclohexane-1,3,5-tricarbonyl chloride; TMC: trimesoyl chloride; MPD: *m*-phenylenediamine).