

A NOVEL NANOFILTRATION MEMBRANE PREPARED WITH PAMAM AND TMC (I)*

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Abstract A series of nanofiltration (NF) membranes were prepared with poly(amido-amine) (PAMAM) and trimesoyl chloride (TMC) *via in situ* interfacial polymerization. The effects of the generation number and concentration of PAMAM on the properties of NF membranes were discussed. Fourier transform infrared spectroscopy (FTIR-ATR), atomic force microscopy (AFM), scanning electron microscopy (SEM) and contact angle measurements were employed to characterize the resulting membranes. The nanofiltration performances were evaluated with solutions of NaCl, Na₂SO₄, MgCl₂ and MgSO₄, respectively. FTIR-ATR spectra indicated that TMC reacted more sufficiently with the higher generation PAMAM. The salts rejection of the resulting membranes increased with increasing the generation number of PAMAM, which was mainly attributed to the concentration difference of terminal amino-groups among the different generation PAMAM. The MgCl₂ (2000 mg/L) rejection of NF-G5 reached 90.3% under the pressure of 0.6 MPa in a cross-flow method measurement. The rejection of MgCl₂ increased with increasing concentration of PAMAM. The salts rejection order of NF membranes with high rejection is MgCl₂ > MgSO₄ > Na₂SO₄ > NaCl. It was also found that the NF-Gx (x = 4, 5, 6, 7) membranes became more hydrophilic with increasing the generation number of PAMAM.

Keywords: PAMAM; TMC; Nanofiltration membrane.

INTRODUCTION

New architectures, whether small molecules or macromolecules, are predicted to produce entirely new properties and behaviors according to Berzelius. The “dendritic polymer architectural state” is no exception^[1]. Dendrimers are constructed in a generation-wise manner starting from a central initiator core molecule. They can be expanded up to the size of macromolecules, however, displaying mono-disperse instead of poly-disperse structures. Therefore, they may show the advantages of polymers, while excluding some substantial disadvantages such as a poor control of molecular shape or limited options for functionalization. The novel physical and chemical properties of dendrimers render these polymers ideal candidates for use in a wide range of applications, such as sensors^[2–5], electroluminescent devices^[6–8], photo-luminescent devices^[9–12], medicine^[13–17], catalysts^[18, 19], analytical chemistry^[20, 21], nano-particles preparation^[22–25] and so on^[26, 27]. In our previous study^[25], the seventh generation poly(amido-amine) (PAMAM) was synthesized and employed to investigate the templation and stabilization effect on the formation of copper nano-particles. To our knowledge, few researches have focused on using dendrimers to prepare filtration or separation membranes^[28], meanwhile, most of these researches studied on the separation of CO₂ from other gases and vapors. For example, Kovvali *et al.* used dendrimers as CO₂-facilitated transporter in polymer films to improve the CO₂ selectivity, the membranes they prepared are immobilized liquid membrane (ILM). However, the ILM is insufficiently tolerant to the large

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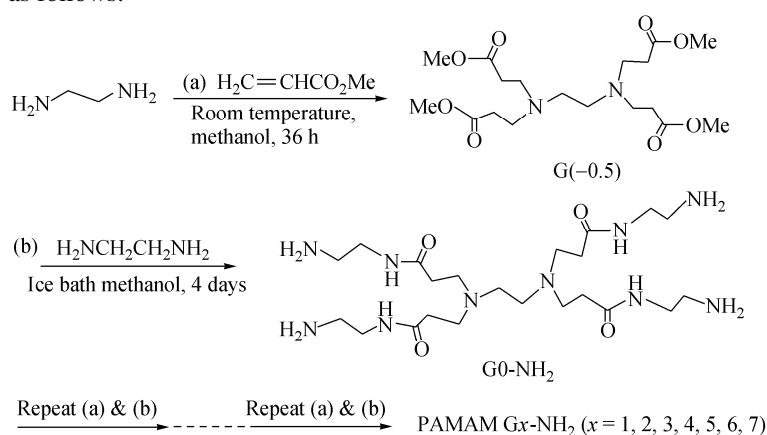
pressure differences required for obtaining sufficiently large gas fluxes. To improve this property, PAMMA dendrimer composite membranes with high CO₂/N₂ selectivity and CO₂ permanence were developed *in situ* according to the *in situ* modification (IM) method. In the study of Tai-shung Chung *et al.*, PAMAM dendrimer generation 0 was employed as a cross-linking agent to modify the polyimide membrane, the membrane was still applied to gas separation. In our study, a series of nanofiltration membranes were prepared with poly(amido-amine) (PAMAM) and trimesoyl chloride TMC.

Nanofiltration (NF) is a pressure-driven membrane separation process that is used for applications such as water softening, brackish water reclamation and dye salt separations. NF membranes consist of a selective skin layer and a highly permeable support. Because of the minimal thickness of the skin layer, it allows a reasonable flux despite its dense nature. Typical procedures for creating such membrane structures include phase inversion, interfacial polymerization^[29–31], grafting^[32] and film deposition on a performed porous support. Recently, researches on preparing NF membranes by adsorption of multilayer polyelectrolyte membranes on polymeric supports were carried out^[33–36]. However, a lot of industrial NF membranes are still prepared by the method of interfacial polymerization. In this case, a polymerization reaction occurs between two very reactive monomers (or one pre-polymer) at the interface of two immiscible solvents. The support layer, which is generally an ultrafiltration membrane, is immersed in an aqueous solution containing a reactive monomer or a pre-polymer, the film is then immersed in a second bath containing a water-immiscible solvent in which another reactive monomer has been dissolved. The two reactive monomers react with each other to form a dense polymeric top-layer^[37]. The monomers dissolved in the water phase usually are piperazine, bisphenol-A, metaphenylene diamine, while the monomers used in the organic phase are often trimesoyl chloride (TMC), isophthaloyl chloride (IC) and terephthaloyl chloride (TC). The objective of present study is to fabricate various nanofiltration membranes with PAMAM and TMC and investigate the effect of generation number of PAMAM on the properties of nanofiltration membranes.

EXPERIMENTAL

Materials

PAMAM was synthesized by means of the procedure described by Tomalia *et al.*^[38] in our laboratory, and the reaction process was as follows:



The ¹H-NMR spectrum of PAMAM G0 was shown in Fig. 1. The ¹H-NMR chemical shifts in different generation PAMAM were shown in our previous article^[39].

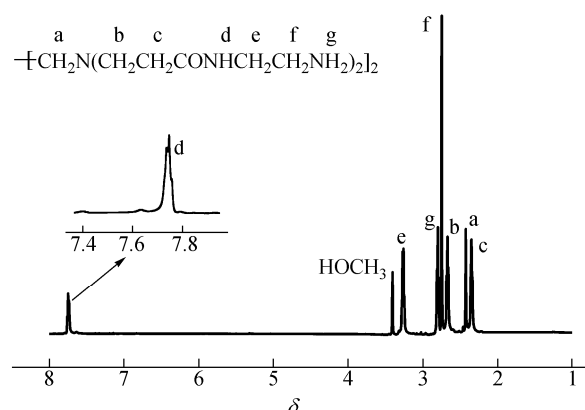


Fig. 1 ^1H -NMR spectrum of PAMAM G0

Other chemicals used were all of AR grade. Trimesoyl chloride (TMC, Aldrich, USA), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), magnesium chloride (MgCl_2), magnesium sulfate (MgSO_4) were purchased from Shanghai Guoyao Factory and used as received. PSf ultrafiltration membranes used as substrate membrane were kindly offered by the Development Center of Water Treatment Technology, State Oceanic Administration (Hangzhou China), which were prepared by casting PSf solution in DMAC on nonwoven polyester fabrics followed by solidification in water. The molecular weight cut-off of these membranes is 3.0×10^4 .

Membrane Preparation

The substrate was immersed in the water phase containing PAMAM (1.05×10^{-4} mol/L) for a while to which 0.05 wt% of sodium dodecylsulfate (SDS) had been added as a surfactant and then was taken out. When the excessive solution was drained off, the membrane was submerged in a 3.75×10^{-3} mol/L solution of TMC in hexane. This resulted in the formation of a thin polyamide film on the micro-porous surface of the PSf UF membrane. The composite membrane obtained then underwent heat treatment in an oven for 10 min at 60°C to attain the desired stability of the formed structure. Finally, the membrane was preserved in water for further use. The PAMAM used ranged from zero to the seventh generation, the resulting membranes were coded as NF-G x ($x = 0, 1, 2, 3, 4, 5, 6, 7$). When the concentration of PAMAM was increased, the resulting membranes were coded as NF-ZG x ($x = 0, 1, 2, 3$). x refers to the generation number.

Membrane Characterization

Fourier transform infrared spectroscopy

Fourier transform infrared spectrometer (FT-IR, Vector 22) with an ATR unit (KRS-5 crystal, 45°) was used to investigate the chemical changes between the substrate and the nanofiltration membranes.

Atomic force microscopy (AFM) and scanning electron microscopy (SEM)

AFM is a powerful asset in characterizing membranes as it allows determination of surface morphology and surface pore size distribution with no special sample preparation. An atomic force microscope (AFM, SPI3800N, Seiko Instrumental, Japan) was used to image the membranes. Membrane morphology was measured in air with a scan rate of 1.00 Hz at 256×256 resolution in tapping mode. The surface and cross-section morphology was also observed by a scanning electron microscopy (SEM, JEOL, JSM-5510LV, Japan).

Characterization of membranes for salts rejection

Nanofiltration experiments were performed at a pressure of 0.6 MPa, in a flat-sheet cross-flow NF test cell with an active membrane area of 23.75 cm^2 (Fig. 2). The membranes were stabilized at 0.8 MPa for at least 30 min with deionized water before testing. NaCl, Na_2SO_4 , MgCl_2 and MgSO_4 salt solutions of 2000 mg/L flowed across the membrane at a rate 0.54 L/min, respectively. NF rejection is defined by Eq. (1):

$$R = (1 - \frac{c_p}{c_f}) \times 100\% \quad (1)$$

where R is the percent solute rejection, c_p and c_f are the concentrations of solute in permeate and feed, respectively.

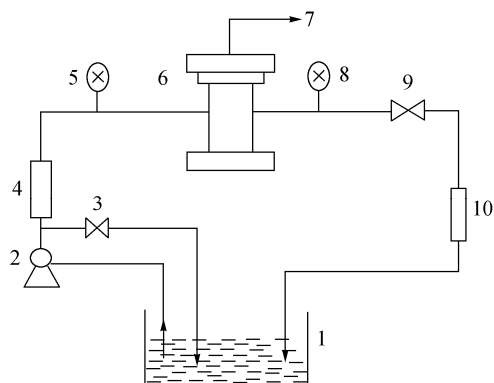


Fig. 2 Schematic representation of the nanofiltration evaluation cell

1) Feed (initial volume: 5 L, temperature 25°C); 2) Feed pump; 3) and 9) valves; 4) Buffer tank; 5) and 8) Pressure gauges; 6) Membrane cell; 7) Permeate end; 10) Flow meter

The flux and rejection were repeatedly measured by collecting filtrate at given periods until stable values of permeation flux and rejection were observed. Values of three membranes were averaged. Salt concentrations in the feed and permeate were determined by using an Electrical Conductivity DDS-11A (Shanghai Leichi Instrument, China).

Water contact angle measurements

Using a sessile drop method, the water contact angle was measured at room temperature on a contact angle goniometer (KRÜSS DSA 10-MK) equipped with a video capture. A total of 1 μ L of deionized water was dropped onto a dry dense membrane with a microsyringe in an atmosphere of saturated water vapor. At least data of 10 contact angle measurements were averaged to get a reliable value.

RESULTS AND DISCUSSION

FTIR-ATR Study

Compared with the PS_f UF membrane, the IR spectrum of NF membranes exhibited evident absorbance signals at 3296 cm^{-1} ($\nu_{\text{N-H}}$), 2921 cm^{-1} and 2843 cm^{-1} ($\nu_{\text{C-H}}$) (Fig. 3). The absorbance signal at 1650 cm^{-1} is assigned to carbonyls in the amido bonds. The similar spectra for PS_f UF were not observed. These data suggested that the active skin layer of the NF membrane was polyamide after *in situ* interfacial polymerization of PAMAM and TMC.

The absorption peak at 3296 cm^{-1} ($\nu_{\text{N-H}}$) increased slightly with increasing the generation number of PAMAM. The signal at 1717 cm^{-1} (assigned to carbonyl in the carboxyl group generated by un-reacted acid chloride) decreased obviously with increasing the generation number. It indicated that TMC reacted more sufficiently with the higher generation PAMAM.

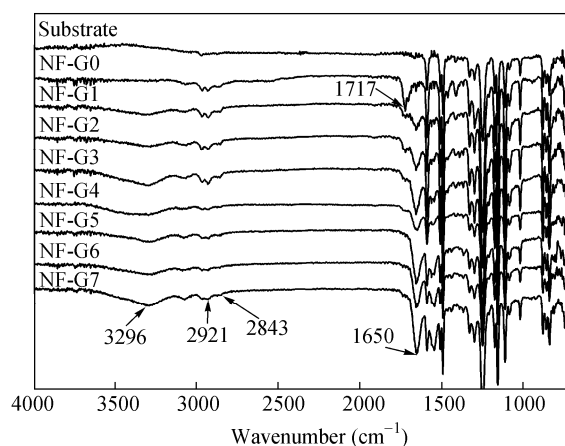


Fig. 3 FTIR-ATR of PSf UF substrate membrane and the studied NF membranes

The Images of Surface Layer

Compared with the substrate membrane, a dense layer was formed on the surface of the NF membranes showing high rejection (Fig. 4 (a-Cross) and (c-Cross)). There were not obvious changes on the surface of the NF membranes showing very low rejection such as NF-G0, NF-G1.

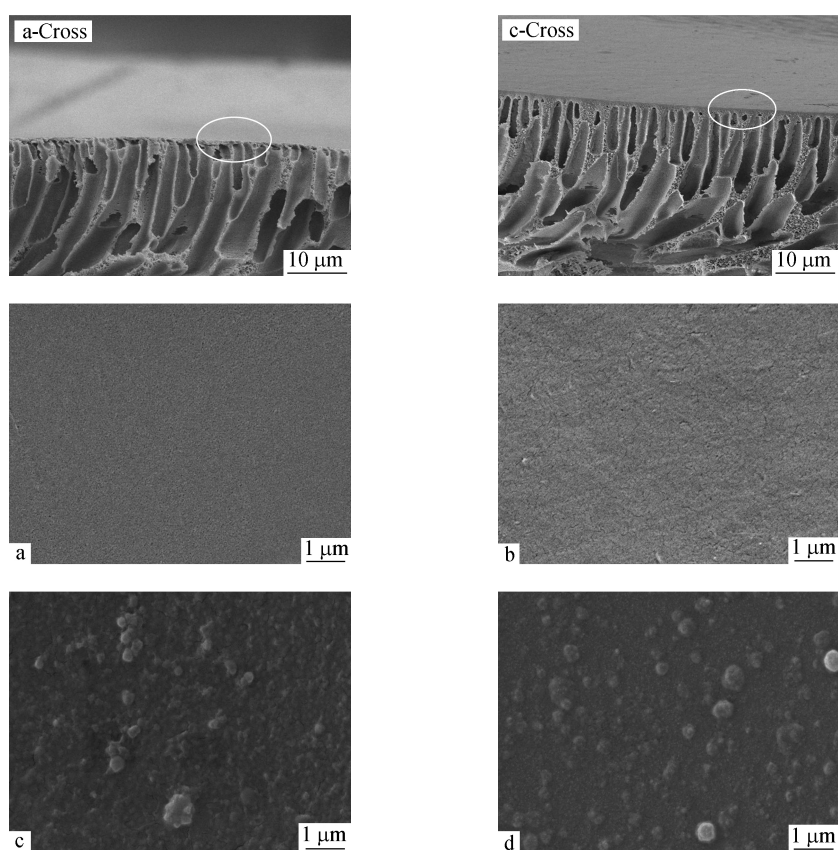


Fig. 4 SEM images of substrate membrane and NF membranes
Cross-section images of substrate membrane (a-Cross) and NF-G4 (c-Cross);
Surface images of (a) substrate membrane, (b) NF-G1, (c) NF-G4 and (d) NF-G5

Figures 4 and 5 showed the SEM and AFM images of the substrate membrane and the typical NF membranes as NF-G1, NF-G4 and NF-G5, respectively.

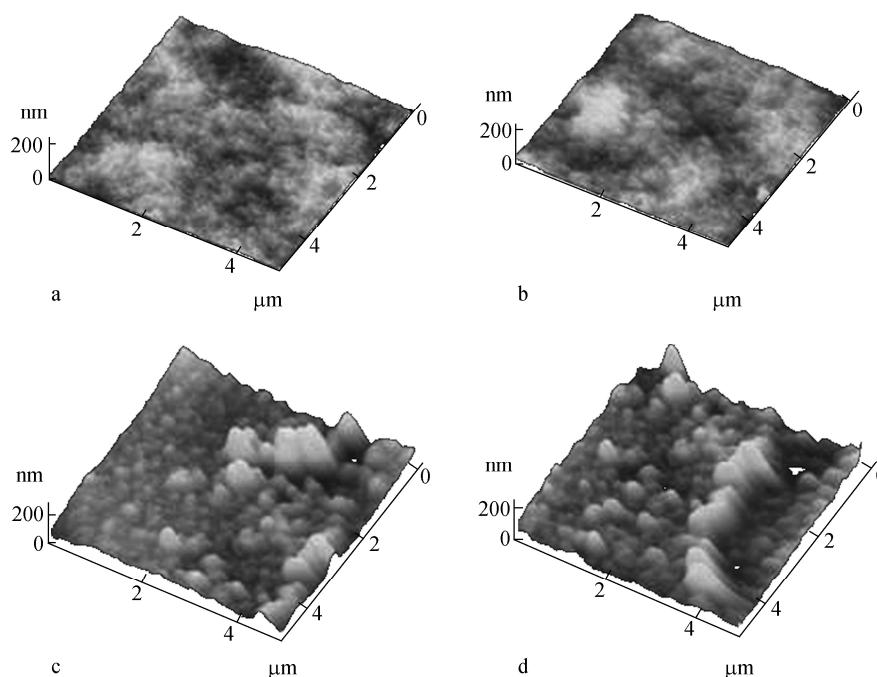


Fig. 5 AFM images of substrate membrane and NF membranes
a) Substrate membrane; b) NF-G1; c) NF-G4; d) NF-G5

The dark regions in the AFM images are depressions and pores, the bright regions are high peaks. Figure 4 shows that after formation of the surface layer, the convex area on the surface increased with the increasing generation number of PAMAM.

Effect of PAMAM Generation Numbers on the Rejection of MgCl_2

Rejection of MgCl_2 for nanofiltration membranes prepared with various generation numbers of PAMAM is shown in Table 1. Rejection of MgCl_2 increased with increasing the generation numbers of PAMAM. Rejection of MgCl_2 for NF-G5 approached 90.3%. This is ascribed to the fact that the concentration of terminal amino-groups in the higher generation PAMAM is higher than that in the lower analogs, thereby TMC reacted more sufficiently with the higher generation PAMAM, and a denser active separation layer is generated. In order to testify it, the concentration of G0, G1, G2, G3 were increased to 16, 8, 4, 2-folds of original concentration, respectively, thereby the concentration of terminal amino groups in the above four PAMAM is equal to that in G4. Table 2 indicated that the rejection of MgCl_2 increased greatly. For example, when the concentration of PAMAM G0 increased from 1.05×10^{-4} mol/L to 1.68×10^{-3} mol/L, the rejection coefficient increased nearly 14-fold.

Table 1. Effect of generation number of PAMAM on the rejection of MgCl_2 (2000 mg/L)

Membrane	NF-G0	NF-G1	NF-G2	NF-G3	NF-G4	NF-G5	NF-G6	NF-G7
R (%)	4.2	7.2	28.1	32.9	86.1	90.3	84.9	89.7
F ($\text{L}/(\text{m}^2\cdot\text{h})$)	332.3	304.5	105.0	144.8	6.6	9.1	6.3	8.4

Concentration of Gx ($x = 0, 1, 2, 3, 4, 5, 6, 7$): 1.05×10^{-4} mol/L

The results (Table 2) also indicated that the topology of different generation PAMAM may has effect on the properties of the NF membrane. For example, NF-G4 and NF-ZG0 were prepared with G4 and G0,

respectively, the concentration of terminal amino-groups in both PAMAM was equal to 6.72×10^{-3} mol/L, the MgCl_2 rejection of NF-G4 was 86.1%, while that of NF-ZG0 was only 69.0%.

Table 2. Rejection of MgCl_2 (2000 mg/L) of NF membranes prepared with PAMAM having same concentration of terminal amino-group

Membrane	NF-G4	NF-ZG0	NF-ZG1	NF-ZG2	NF-ZG3
R (%)	86.1	69.0	78.2	79.9	86.6
F ($\text{L}/(\text{m}^2 \cdot \text{h})$)	6.6	21.7	16.3	16.9	8.8

Concentration of G_x ($x = 0, 1, 2, 3, 4$) were 1.68×10^{-3} , 8.4×10^{-4} , 4.2×10^{-4} , 2.1×10^{-4} and 1.05×10^{-4} mol/L, respectively; Concentration of terminal amino group: 6.72×10^{-3} mol/L

Rejection of Different Salts for Nanofiltration Membranes

Figure 6 and Table 3 showed that the salts rejection order of membranes NF-G x ($x = 0, 1, 2, 3, 4$) is $\text{MgCl}_2 > \text{MgSO}_4 > \text{NaCl} > \text{Na}_2\text{SO}_4$, which shows a typical retention sequence for positively charged membrane. While the membranes NF-G x ($x = 5, 6, 7$) and membranes NF-ZG x ($x = 0, 1, 2, 3$) show different rejection order as $\text{MgCl}_2 > \text{MgSO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$. Most authors agree that ionic transport and selectivity of NF membranes mainly (but not exclusively) depended on two effects. The first one is caused by the charged nature of the membrane and the electrolyte, the second one is caused by the relative size of ions to the membrane pores. For the same kind of anion Cl^- or SO_4^{2-} , the rejection coefficient of divalent cation is higher than that of the monovalent one. For example, the rejection coefficient of MgCl_2 is higher than that of NaCl , and the rejection coefficient of MgSO_4 is higher than that of Na_2SO_4 . This order can be explained by the Donnan exclusion. However, the rejection of Na_2SO_4 is higher than that of NaCl , which may be attributed to the fact that the hydration ion radius of SO_4^{2-} is larger than that of Cl^- ^[40], the sieving effect also plays an important role.

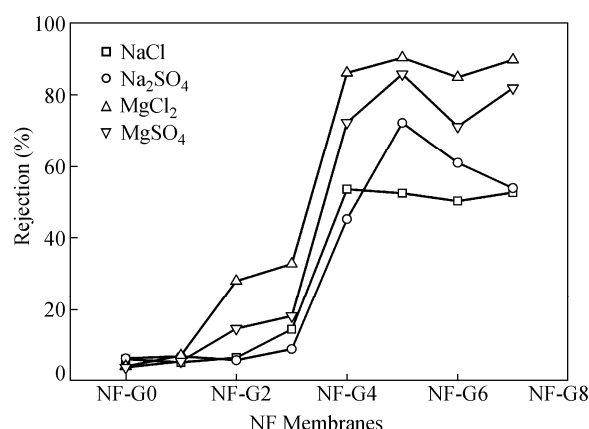


Fig. 6 Effect of generation numbers on the rejection of different salts

Table 3. Rejection of different salts of NF membranes prepared with PAMAM having same concentration of terminal amino-group

	NaCl		Na ₂ SO ₄		MgCl ₂		MgSO ₄	
	R (%)	F ($\text{L}/(\text{m}^2 \cdot \text{h})$)	R (%)	F ($\text{L}/(\text{m}^2 \cdot \text{h})$)	R (%)	F ($\text{L}/(\text{m}^2 \cdot \text{h})$)	R (%)	F ($\text{L}/(\text{m}^2 \cdot \text{h})$)
NF-ZG0	32.2	20.2	60.2	21.1	69.0	21.7	64.9	22.5
NF-ZG1	40.3	14.4	67.7	15.2	78.2	16.3	73.8	17.9
NF-ZG2	39.0	13.3	50.4	14.4	79.9	16.9	73.1	17.6
NF-ZG3	43.7	6.6	74.7	6.9	86.6	8.8	82.9	9.9

Concentration of G_x ($x = 0, 1, 2, 3$) were 1.68×10^{-3} , 8.4×10^{-4} , 4.2×10^{-4} and 2.1×10^{-4} mol/L, respectively; Concentration of terminal amino group: 6.72×10^{-3} mol/L

Table 3 and Fig. 7 showed the flux of the resulting nanofiltration membranes, which indicated that the flux decreased obviously with increasing the generation number of PAMAM except NF-G3.

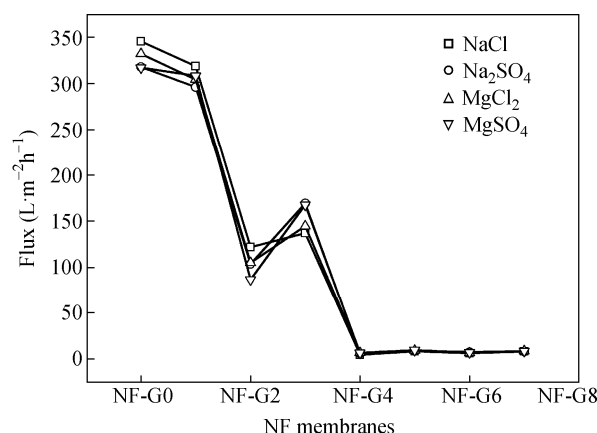


Fig. 7 Effect of generation numbers on the flux of different salts

Stability-Test of Nanofiltration Membranes

The short-term stability-test was carried out at 0.6 MPa with 2000 mg/L MgCl_2 on NF-G x ($x = 4, 5, 6$) for a week, respectively. The membranes were allowed to be equilibrated with the flowing solution for 60 min, and permeate aliquots were collected every 60 min for 144 h. The fluxes and rejections of NF-G4 membrane during the 144 h of filtration were shown in Fig. 8. There was no significant change in flux or rejection. These results demonstrate that the studied NF membrane show good stability in the application.

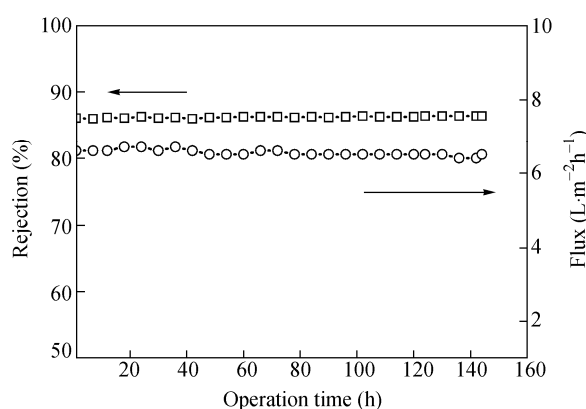


Fig. 8 Short-term stability test of NF-G4 membrane

Contact Angle of Different PA Nanofiltration Membranes

The contact angle of NF-G x ($x = 0, 1, 2, 3$) changed irregularly, while that of NF-G x ($x = 4, 5, 6, 7$) decreased with increasing generation number (Table 4). Surface contact angle depended on many effects as hydrophilicity of the surface substance, roughness of the surface and so on.

Wenzel^[41] suggested that roughness has a major impact on the contact angle. He explained the relationship between the roughness of a nonporous surface and the contact angle. While Cassie and Baxter explained the wetting behavior of porous surfaces (having both liquid-air and liquid-solid interfaces), such as feathers and fabrics, and they proposed that at high levels of roughness, a fluid would sit primarily on the air contained in the pores of the rough material. They derived an Eq. (2), where $\cos\theta^{\text{porous}}$ is the apparent contact angle, f_1 is the fraction of fluid area in contact with the material, and f_2 is the fraction of the fluid area in contact with air in the porous material.

$$\cos\theta^{\text{porous}} = f_1 \cos\theta - f_2 \quad (2)$$

Johnson and Dettre predicted that a surface should translate sharply from a nonporous (Wenzel regime) to a porous surface (Cassie regime) as the roughness increases.

Table 4. Contact angle of substrate membrane and NF membranes

Membrane	Contact angle (°)	Membrane	Contact angle (°)
NF-G0	71.9 ± 1.4	NF-G4	89.6 ± 1.8
NF-G1	93.3 ± 1.1	NF-G5	82.9 ± 1.8
NF-G2	95.5 ± 1.3	NF-G6	62.5 ± 2.3
NF-G3	77.5 ± 1.6	NF-G7	56.6 ± 1.5

Contact angle of substrate membrane: 95.4° ± 2.4°

The surface of the nanofiltration membranes is a composite surface; many authors agreed that the selective surface layer is composed of nanometer pores^[42]. Compared with NF-Gx ($x = 0, 1, 2, 3$) membranes, the surface of NF-Gx ($x = 4, 5, 6, 7$) were more sufficiently covered by hydrophilic polyamide generated by the reaction of PAMAM and TMC, which can be testified by the SEM (Fig. 4) and AFM images (Fig. 5). The results of salt rejection (Fig. 6) and flux (Fig. 7) can also indicate it. Meanwhile, for NF-Gx ($x = 4, 5, 6, 7$) membranes, the number of the amino groups un-reacted with TMC increased with increasing the generation number, which in water were able to changed to RH_3N^+ because of the combination of the lone electron pair on N and water. Therefore, the contact angle decreased with increasing the generation number. Herein, the contact angle of NF-Gx ($x = 0, 1, 2, 3$) changed irregularly, and the detail reason needs to be understood.

CONCLUSIONS

A series of NF membranes were prepared with PAMAM and TMC *via in situ* interfacial polymerization. Effects of the generation number and concentration of PAMAM on the properties of NF membranes were investigated. FTIR-ATR spectra indicated that TMC reacted more sufficiently with higher generation PAMAM, which is favorable to build a dense top-layer on the base membrane. Therefore the rejection of NaCl, Na_2SO_4 , MgCl_2 , and MgSO_4 increased with increasing the generation number, respectively. The rejection of salts also increased with increasing concentration. The salts rejection order of membranes with high rejection coefficient is $\text{MgCl}_2 > \text{MgSO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$. The combined effect of the Donnan exclusion and sieving effect may explain the obtained results. Taking into account the preparation cost, the intermediate generation PAMAM with higher concentration is recommended in the future NF preparation.

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