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Effects of polymerization conditions on hydrophilic groups in aromatic polyamide thin films

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ABSTRACT

For polyamide used in reverse osmosis (RO) membranes, the content of pendant acid groups is critical to its performance. In this work, FTIR was used to analyze the acid contents in the polyamide films prepared via interfacial polymerization of trimesic acid trichloride (TMC) in hexane and 1,3-phenylenediamine (MPDA) in water, and the effects of reaction conditions, including monomer concentrations, time, and temperature, were studied. It was found that more pendant acid groups are present in the polyamide film at higher TMC concentrations or lower MPDA concentrations, and longer reaction times and lower temperatures also favor the formation of the free acids. These results can be explained by the monomer diffusion in the interfacial polymerization process. This work may help the design and fabrication of RO membranes with different hydrophilicity and target performance.

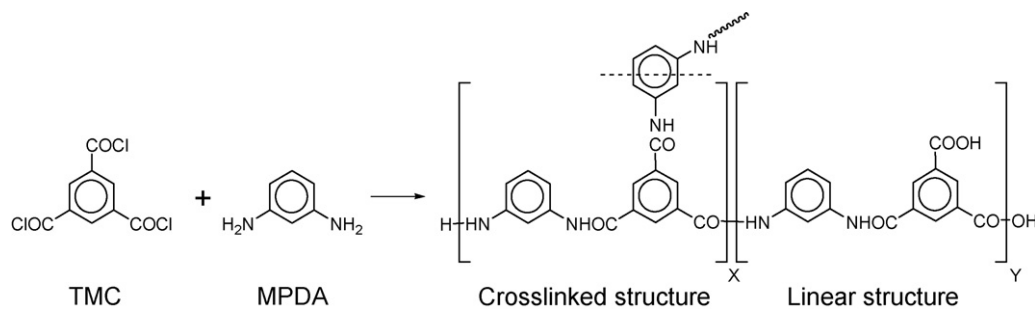
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1. Introduction

Reverse osmosis (RO) membranes are widely used in desalination and industrial water treatment. In addition, RO membranes are finding applications in a variety of other separation operations in the environmental, chemical, and food industries [1–3]. For these applications developing membranes with high water flux is the focus. The demand for higher fluxes for more economic profits rests with the “active layer” in these membranes, which is a polymeric dense thin film attributing the permselectivity, the separation of components from the feed raw water [4]. In commercially successful thin-film-composite (TFC) membranes, most of the thin-film polymers are aromatic polyamides [5]. The aromatic polyamide active layer synthesized via interfacial polymerization (IP) of amine in aqueous phase and multifunctional acid chloride in organic phase shows the desired combination of water flux and solute rejection [4,5,16]. In the IP process, the immiscible aqueous and organic phases are brought together without stirring and an insoluble thin polymer film is formed immediately in between the two phases [6]. The reaction takes place at the organic side of the interface due to the negligible solubility of acid chlorides in water and the fairly good solubility of amines in organic solvents, and so the film grows into the organic phase [7–10]. After the IP reaction between

the amine and the acid chloride occurs for a short time, the film increases very slowly, due to the formation of a dense crosslinking barrier, reported as “self-limiting”, which would block the diffusion of the amine [6,7,11]. Based on this principle, Rozelle et al. [12] and Cadotte [13] developed the IP technique for manufacturing TFC RO membranes in 1972. The TFC RO membrane consists of three structural components: polyester fabric, polysulfone support, and polyamide dense film layer. The reaction conditions such as temperature, reaction time, monomer concentrations, and concentration ratio all play an important role in determining the structure of the IP film [14]. In these RO membranes, higher water flux was attributed mainly to higher hydrophilicity (arising from the carboxylic acid structure formed by the hydrolysis of the acyl chloride groups) of the aromatic polyamides [4,14]. The increased negative charges of the network polyamide due to the presence of the carboxylic acid groups are indirect effects but greatly impact water flux as well as rejection [4]. Hydrophilicity was found to overwhelm other factors such as film thickness, density, free-volume, polymer chain mobility, and polymer–solvent/polymer–solute interactions [4]. Therefore, it is critical for the performance of the RO membranes to control the functional groups in the active layer. However, in the IP synthesis process, either of the two reagents (the amine and the acid chloride) in excess would change the concentration of the end groups and disrupt the homogeneity of the thin film [15], and so far in the literature there is still little information on controlling the active layer structure under different reaction conditions. In addition, the polyamide dense active layer in the TFC RO membranes is difficult to characterize because the dense layer is

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Scheme 1. The IP reaction.

both insoluble and very thin. As the performance and efficiency of the RO process primarily depend on the nature of the polyamide active layers [4,14,16,17], a systematic study is needed in order to establish correlations between different reaction conditions and the chemical structures, which will then help guide the molecular structure design and synthesis of RO membranes with different hydrophilicity and target performance.

The interfacial polymerization is very fast and the film produced is extremely thin growing at the interface between the organic and the aqueous phases, so it is difficult to study by traditional methods. In this report we synthesized free active polyamide films under various reaction conditions and studied the films by FTIR to determine the influence of the reaction conditions to the structure of the aromatic polyamide films.

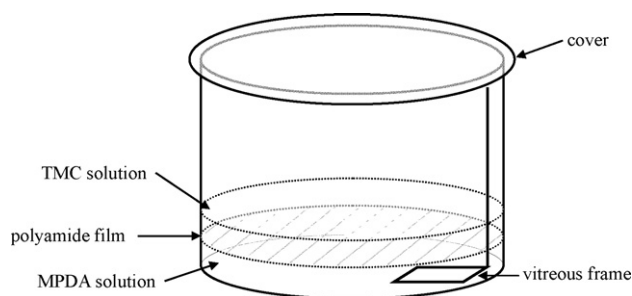
2. Experimental

2.1. Materials

The network polyamide (poly(metaphenylene trimesamide), MPTA) was synthesized from trimesic acid trichloride (TMC) and 1,3-phenylenediamine (MPDA). TMC (98%, Aldrich) was distilled under vacuum at 160 °C, and the purified TMC was stored in vacuum desiccator prior to use to prevent hydrolysis of the acyl chloride. MPDA (99%, Aldrich) was distilled under vacuum at 170 °C and the purified form was filled in a dark bottle under N₂ protection and stored in a desiccator. The solvent for acyl chlorides was n-hexane. For the preparation of the diamine solution, RO purified and deionized water was used. The interfacial reaction between TMC and MPDA is shown in Scheme 1.

2.2. IP film preparation

In the IP reaction, the reactants were in two mutually insoluble phases: the amine aqueous phase and the acyl chloride organic phase. When a specified amount of the TMC organic solution was carefully added within several seconds to a predetermined amount of the MPDA aqueous solution, the reactants diffused and reacted at



Scheme 2. The experiment of IP reaction.

the interface via a polycondensation reaction to produce an unsupported polyamide thin film (Scheme 2). The two phases were not disturbed until a sample of the IP film was collected. The amounts of both the aqueous and the organic phases used in each experiment were maintained nearly constant. Part of the thin IP polyamide film was slowly taken out using a vitreous frame, and washed immediately with pure n-hexane, deionized water, and methanol for three times each to remove the unreacted monomer remnants and occluded salt. Then the sample was dried under vacuum at 45 °C to remove the solvent completely.

The parameters chosen for this study were MPDA concentration, TMC concentration, contact time, and temperature. Four series of polyamide thin films were prepared (Table 1).

2.3. Analytical method

The films were analyzed on a Bruker Vertex 70 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The spectra were collected at 4 cm⁻¹ resolution and 64 scans, and were baseline-corrected using the OPUS software. Curve fitting was performed using the Levenberg–Maquardt least-squares algorithm routine of the OPUS software package, and the residual rms error was about 0.005.

The morphology of the IP film was investigated using an FEL XL30 ESEM field emission scanning electron microscope. A thin layer of Au was coated on the film surface prior to SEM observation.

3. Results and discussion

The polyamide active layer in commercial TFC RO membranes typically is produced directly on porous polysulfone sponge support layer, which is too thin to peel off or to characterize in situ. Therefore in this study we fabricated free standing polyamide films using

Table 1
Summary of the reaction conditions for the preparation of the aromatic polyamide films.

	TMC (wt/v%)	MPDA (wt/v%)	Reactant ratio (MPDA/TMC)	Temperature (°C)	Time (min)
Series I	0.5	4	8	50	20
	1		4		
	2		2		
Series II	1	2	2	50	20
		4	4		
		8	8		
Series III	2	4	2	65	0.5
					2
					5
					10
					20
Series IV	1	4	4	35	20

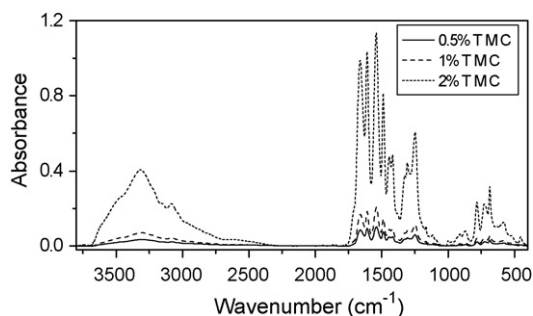


Fig. 1. Infrared spectra of the polyamide films prepared at different TMC concentrations (at 50 °C, 4% MPDA concentration, and 20 min reaction time) (Series I).

same monomers and similar reaction conditions as that reported in the literature [15,21,23]. In order to investigate the four parameters expected to influence the IP reaction, which are MPDA concentration, TMC concentration, contact time, and temperature, four series of IP reactions were carried out, the conditions of which are listed in Table 1. The FTIR spectra of the aromatic polyamide films prepared at various TMC concentrations when the MPDA concentration, reaction time and temperature all remain constant are displayed in Fig. 1 (Series I). The infrared characteristics of the polyamide films are similar to that of the IP layer in TFC membranes [15,21,22], indicating that their chemical compositions are largely the same, which is not surprising since they were synthesized from the same monomers under similar conditions. It can be seen that the absorbance in the whole spectral range increases with the TMC concentration, apparently as a result of the increase in film thickness. This suggests that the thickness of the polyamide film can be conveniently controlled by adjusting the concentration of the TMC in the organic phase. The film thickness was found to depend on the MPDA concentration in the aqueous phase while all other conditions remain constant (see Supplemental Information). In the spectra the vibrational bands characteristic of amide functionalities are present at 3540 cm^{-1} (free N–H stretching vibration), 3305 cm^{-1} (bond N–H stretching vibration), 3074 cm^{-1} (amide II overtone), 1660 cm^{-1} (amide I) and 1540 cm^{-1} (amide II) in addition to the aromatic ring breathing band at 1608 cm^{-1} , which clearly indicate that the interfacial polymerization has occurred. Since TMC is trifunctional, the reaction between diamines and trimesoyl chloride can lead to two types of structures simultaneously [12,18], which are the totally crosslinked units when the acid chlo-

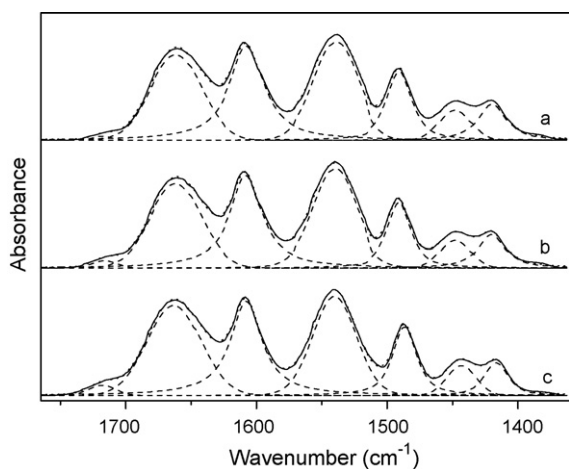


Fig. 2. The 1350–1750- cm^{-1} region of the infrared spectra of the polyamide films of Series I: (a) 0.5% TMC, (b) 1% TMC, and (c) 2% TMC. The dotted lines are the deconvoluted peaks, and the dash lines are the fitted curves.

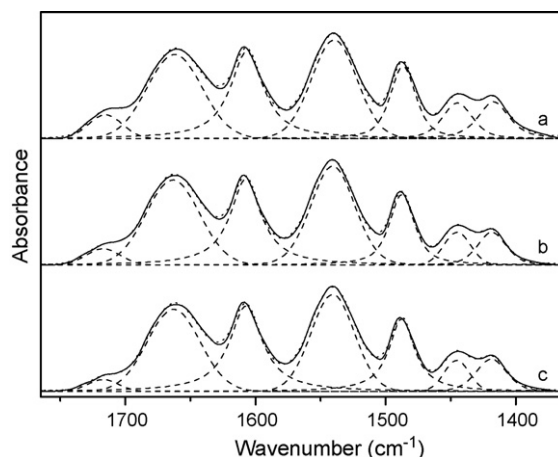


Fig. 3. The 1350–1750- cm^{-1} region of the infrared spectra of the polyamide films prepared at different MPDA concentrations (Series II, at 50 °C, 1% TMC concentration, and 20 min reaction time): (a) 2% MPDA, (b) 4% MPDA, and (c) 8% MPDA. The dotted lines are the deconvoluted peaks, and the dash lines are the fitted curves.

ride group of an available branch reacts with an amine group of another chain, and a linear structure with a pendant carboxylic acid from the hydrolysis of one acyl chloride group of the trimesoyl chloride that gives the PA film an appreciably acidic character [12] when the ratio of MPDA/TMC is 1 approximately. In all three spectra, the vibrational band at 1720 cm^{-1} assigned to the C=O stretching of carboxylic acids are clearly identified, indicating the presence of pendant carboxylic acid groups in the polyamide films.

To better understand the effects of TMC concentration, the 1350–1750 cm^{-1} region of the FTIR spectra, where the vibrational bands of interest are present, is displayed in Fig. 2. To separate the partially overlapped bands, curve fitting was performed so that each component can be identified. The 1720- cm^{-1} band characteristic of the pendant carboxylic acids was employed as a quantitative indication of the acid content in the polyamide film, while the amide II band at 1540 cm^{-1} was taken as a reference, because as we just discussed the film thickness is dependent on the TMC concentration. It can be seen that the relative intensity of the 1720- cm^{-1} band with respect to the amide I band increases with the TMC concentration. On the other hand, the spectra in the same region of the polyamide films prepared at various MPDA concentrations while the TMC concentration, reaction time and temperature all remain constant are shown in Fig. 3 (Series II). It can be seen that the relative intensity of the carboxylic acid band at 1720 cm^{-1} decreases with the increase of the MPDA concentration in the aqueous phase. These results suggest that higher TMC concentration in the organic phase or lower

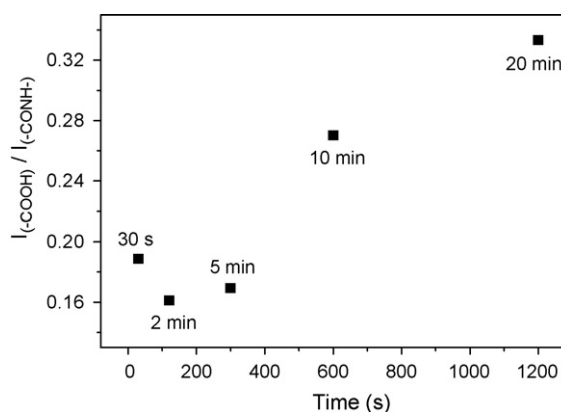


Fig. 4. Acid content in the polyamide film as a function of the reaction time (Series III, with 2% TMC reacts with 4% MPDA at 65 °C).

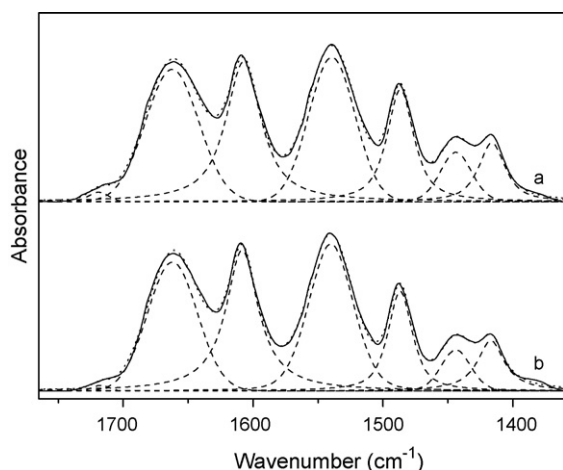


Fig. 5. The 1350–1750-cm⁻¹ region of the infrared spectra of the polyamide films prepared at different reaction temperatures (Series IV, at 1% TMC and 4% MPDA, and 20 min reaction time): (a) 35 °C and (b) 45 °C. The dotted lines are the deconvoluted peaks, and the dash lines are the fitted curves.

MPDA concentration in the aqueous phase leads to higher contents of carboxylic acid functionalities in the polyamide film. When the MPDA concentration in the aqueous phase is higher, more MPDA molecules are likely to diffuse to the aqueous/organic interface and the growth front of the film; the MPDA/TMC ratio at the interface is greater, and crosslinked units are more likely to be produced, resulting in lower contents of linear structure with pendant -COOH groups in the polyamide film. On the other hand, higher TMC concentrations provide more TMC molecules at the organic side of the interface where the film grows, resulting in more unreacted acid chloride groups and hence higher contents of -COOH in the film.

To study the effects of reaction time on the composition of the polyamide film, the reaction was carried out at 65 °C (Series III). This temperature was chosen because at higher temperatures the diffusion of monomers is fast [19,20] and thicker films are produced, which makes the removal and subsequent characterization of the films easier. The acid content in the film indicated by the IR band intensity at 1720 cm⁻¹ relative to the amide I band at 1660 cm⁻¹ as a function of the reaction time is shown in Fig. 4. It can be seen that when the reaction time increases, the acid content in the film first quickly decreases to reach a minimum, and then increases steadily. This may be attributed to the “self-limiting” in the reaction process. In the early stage, MPDA molecules diffuse to the organic side of the interface to react with the TMC to produce the initial polyamide film with many pendant acid chlorides; these acid chlorides can then react with more incoming MPDA monomers, resulting in a denser and more crosslinked film with a lower acid content. Then for the film to grow, MPDA molecules have to diffuse through this

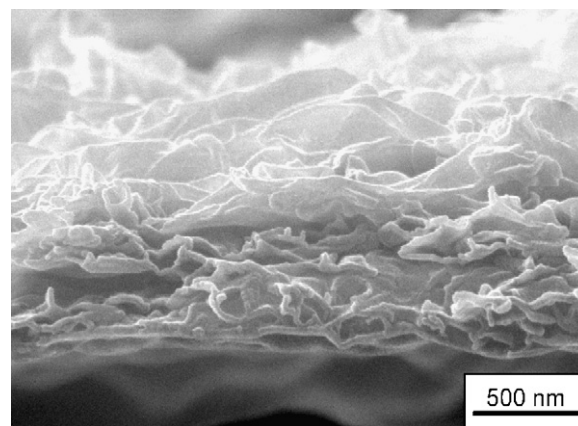


Fig. 7. FE-SEM micrograph of the cross section of the polyamide film.

polyamide film to the organic/film interface, which is slow compared to the diffusion of TMC from the bulk solution to the interface, so that in the polymerization process TMC is in excess and more linear amide units with pendant acid group are produced. At longer reaction times, the film is thicker, and the MPDA diffusion is more difficult and more residual acid groups are resulted from the excess TMC.

The effect of temperature is shown in Fig. 5 (Series IV). We can see that the acid content in the film is lower when the reaction temperature is higher. This is because temperature influences the diffusion of the two monomers, especially the diffusion of MPDA, which is more difficult as discussed above. The magnitude of the instantaneous monomer fluxes to the reaction front play a pivotal role in determining the structure of the eventual network [12]. At higher reaction temperatures, more MPDA monomers will transport through the film to the organic/film interface and react with the TMC monomers, and the higher MPDA/TMC ratio results in lower content of pendant acids in the film produced.

In addition, the polyamide film was examined by electron microscopy. The surface morphology of the film is shown in Fig. 6. It is distinct that the amorphous film possesses two different surfaces, a coarse surface with large holes exposed to the organic phase and a smooth, dense, porous surface exposed to the aqueous phase. In the IP process, the reaction front where the film grows is at the organic/film interface, and the surface tension of the organic solvent is much smaller than that of water. These might be the reasons that the surface exposed to the organic phase is more coarse. Furthermore, by examining the cross section of the film (Fig. 7), we can see that the IP film has a porous structure and its thickness is around 500 nm. The morphology is similar to that of the polyamide active layer in TFC RO membrane [15,19,22,23].

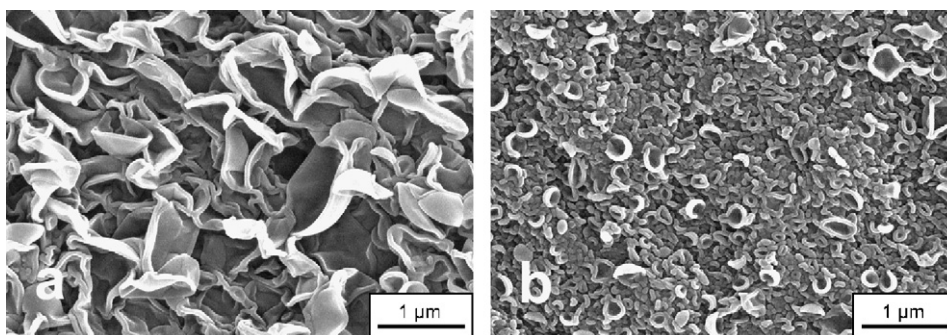


Fig. 6. FE-SEM micrographs of the polyamide film surfaces exposed to the organic phase (a) and to the aqueous phase (b).

4. Conclusions

In this work, free standing films of the active crosslinked skin layer of thin film composite membranes for the reverse osmosis process were prepared by interfacially reacting TMC with MPDA. The effects of reaction conditions, including MPDA and TMC concentrations, contact time and temperature, on the content of the carboxyl groups which is critical to the performance of the membrane were investigated. The results show that the variations in the TMC and MPDA concentrations have pronounced effects on the hydrophilicity (–COOH) of the PA thin film, and the structure of the PA films changes with the reaction time. The temperature increases the diffusion rate of MPDA monomers to pass through the interface and has great effect on the IP reaction. This work provides an improved basis for understanding the relationship between the reaction conditions and the chemical structure of the resulting PA films, which may help the design and synthesis of commercial TFC RO membranes with better performance.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2008.12.055.

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