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Synchrotron SAXS to probe cross-linked network of polyamide ‘reverse osmosis’ and ‘nanofiltration’ membranes

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ABSTRACT

A typical ‘reverse osmosis’ (RO) or ‘nanofiltration’ (NF) polyamide cross-linked structure is formed by interfacial reaction between an aqueous solution of *m*-phenylene diamine (or piperazine) and a trimesoyl chloride solution in *n*-hexane. Using synchrotron SAXS, it was observed that a little change in the reactant concentrations resulted to different cross-linked networks of the polyamides. A clear difference between the cross-linking networks of RO and NF polyamides was observed even though there were some similarities in terms of the nature of polymer chain compaction and the cluster formation by aggregation. In both the polyamides, there was strong compaction of polymer chains forming globular like objects having smooth interface which was well deviated from the Gaussian polymer chain nature ($I \propto Q^{-2}$) wherein the NF polyamide had relatively more compaction with Porod scattering $I \propto Q^{-3.8}$ than $I \propto Q^{-3.4}$ of the RO polyamide. The size of the compacted globules containing about 1400 trimesamide monomeric units for the NF polyamide was slightly smaller than that of the RO polyamide. These globules were very strongly aggregated to form polymer nodules. The nodular cluster size for the NF polyamide was ~2000–3000 Å which was ~6–7 times larger than that of RO polyamide. These differences in the nature of polymer chain compaction and the cluster size agreed with the differences in effective cross-link density measured by equilibrium swelling in dimethyl acetamide and the polymer nodule sizes observed by the AFM.

1. Introduction

Thin-film composite (TFC) membranes comprised of a top polyamide layer, a middle porous polymer support and a bottom reinforced fabric are state-of-the-art membranes which are currently employed for numerous reverse osmosis (RO) and nanofiltration (NF) separation processes [1,2]. The top polyamide layer, which is responsible for high flux and selective separation, is an ultrathin layer of about 100–200 nm formed by an interfacial polymerization technique. Depending upon the type of monomers used in the interfacial polymerization, the properties of membrane can be tuned. Generally, the polyamide formed from the polymerization of *m*-phenylene diamine and trimesoyl chloride monomers give the reverse osmosis (RO) membrane [3–5] type properties while the polymerization of piperazine (PIP) and trimesoyl chloride monomers give the nanofiltration (NF) membrane type [6,7] properties. These membranes provide an effective solution for producing potable fresh water from saline and waste water.

The RO polyamide membranes which have non-interconnecting pores [8] can reject (~99%) all the electrolytes present in saline water while the NF polyamide membranes, which have slightly larger pores [9] can selectively reject larger ions or molecules such as divalent electrolytes, dyes, proteins etc. Hence, RO membranes are used for producing fresh water from brackish ground water and sea water whereas the NF membranes are suitable for water reclamation, purification, and hardness removal as well as in the treatment for various environmentally hazardous aqueous effluents. Since fresh water is required for domestic uses, agricultural irrigation and industrial processes, continuous improvements of the membranes are required to meet the increasing fresh water demands needed by population growth and industrialization. In order to develop membrane with improved performance, the polyamide membrane structure should be fine-tuned with the desired properties. For TFC membranes, the top polyamide membrane layer is principally responsible for permeability and selectivity. The polymerization of polyamide film formation is a rapid process that the membrane thickness of over 500–2000 Å is quickly formed within a few seconds of reaction. As the polyamide formed is not completely soluble in organic solvents because of its cross-linked structure, understanding of the size and structure of the macromolecular

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units of polyamide networks that constitute thin membrane film has been difficult.

Various analytical techniques have been used to characterize the polyamide membranes mentioned above. For example, ATR-IR [10–12], AFM [13–16], NMR [15–17], TEM [18], ESR [19], XPS [20,21], and XPS cum Rutherford backscattering spectrometry (RBS) [22] have been used to characterize the membrane thickness, surface and chemical functional groups. The small-angle scattering has been used for structural understanding of the polyamide membrane at micrometer and nanometer length scale using X-rays [23] and neutrons [24] over the scattering wave vector range 0.0006–0.04 $Å^{-1}$ and 0.018–0.35 $Å^{-1}$ respectively. The small angle scattering technique reveals the internal features of the polyamide membranes. The X-ray scattering was performed on the polyamide film after isolating the top polyamide film from the base layers of the TFC membrane. [23] The X-ray scattering profiles over the micrometer length scale 150–10500 Å provided information on the fractal surfaces of large structure of the cross-linked polyamide. The results indicated that polyamide film is constituted of close packing of globular structural units. On the other hand, the neutron scattering over the nanometer length scale 20–350 Å provided information on the smaller globular units forming the large fractal structures. The size of globules were found to be about 120–130 Å as observed by the neutron scattering measurements from polyamides in dilute solution system after collecting the immediately prepared thin films in water containing large amounts of D_2O [24].

In the present work, we recorded Synchrotron X-ray scattering data of the polyamides over the scattering wave vector 0.003–1.5 $Å^{-1}$ corresponding to 4.2–2094 Å length scale for mapping of total scattering data in order to elucidate the cross-linked network structure of the membranes. The scattering data would be from the molecular units, the primary building units and large fractal structures constituted by the primary units The Synchrotron X-ray can collect statistically reliable data for polymers within seconds because of its extremely high X-ray intensity as compared to the long hours of neutron scattering measurement time.

The cross-linked network structure of the polymer film is formed by interfacial reaction between monomers which are diffused from both organic and aqueous phases. Therefore the film characteristics would be dependent on the total number of monomers participated in the reaction. Effects of reactant concentration and solution volume on structure of the cross-linked RO and NF polyamide were studied using the Synchrotron SAXS.

2. Experimental

2.1. SAXS experiments and data analysis

A specific volume of clear aqueous solution containing *m*-phenylene diamine (for RO type polymer) or piperazine (for NF type polymer) was injected in a cylindrical cell. A specific volume *n*-hexane solution containing trimesoyl chloride will then transferred to the above aqueous solution slowly and allowed to react for 40 s. Thin film formation was observed at the interface of water and organic phase. Immediately, the solvents (water and organic) were poured out while keeping the polyamide film in the cylindrical cell. The film was then rinsed with deionised water. As the film was thin and unsupported, it was mechanically weak and easily broken into fine flaky particles and dispersed in water. These fine particles were highly swelled and floated in water and they were then transferred into the quartz capillary of 1.5 mm diameter for the synchrotron X-ray scattering measurements at the Australian synchrotron beam line at Melbourne, Australia. The scattering angle ranges were adjusted by two camera length settings (0.56 m, $Q=0.03$–1.5 $Å^{-1}$ and 3.3 m, $Q=0.003$–0.18 $Å^{-1}$) for 12 KeV beam (1.0322 Å wavelength). Acquisition time of 2 s was used for all samples. The scattered X-ray intensity of the sample was corrected by computing the intensity data of both sample and background scattering.

The polymer film is formed by diffusion of monomers from both organic and aqueous phases. Therefore the film characteristics depend on the total number of monomers participated in the reaction which are determined by monomer concentration and solution volume. The starting reactant concentrations used in the study are within the typical concentration ranges used for preparation of the standard RO and NF membranes [25–27]. As given in Table 1, the RO samples RO111, RO112 and RO113 had the same aqueous *m*-phenylene diamine solution concentration but different trimesoyl chloride concentration of the *n*-hexane solution while RO111, RO121 and RO131 had same trimesoyl chloride concentration but different *m*-phenylene diamine concentration. For these samples, the trimesoyl chloride and *m*-phenylene diamine solution volumes were kept constant (50 ml). To study the effect of the organic solution volume (wherein the polymerization takes place), the organic solution volumes for RO211 and RO311 samples were reduced to two-fifth and one-fifth of the normal preparation, respectively. Similarly, a series of the NF sample were prepared for comparison studies. Aqueous PIP solution instead of *m*-phenylene diamine solution

Table 1
Details of reactant solution concentrations and volumes for preparation of RO and NF polyamides.

	Trimesoyl chloride (ml)	*m*-phenylene diamine (ml)	Trimesoyl chloride (wt%)	*m*-phenylene diamine (wt%)
RO series				
RO111	50	50	0.1	2
RO112	50	50	0.2	2
RO113	50	50	0.05	2
RO121	50	50	0.1	0.5
RO131	50	50	0.1	0.1
RO211	20	50	0.1	2
RO311	10	50	0.1	2
	Trimesoyl chloride (ml)	Piperazine (ml)	Trimesoyl chloride (wt%)	Piperazine (wt%)
NF series				
NF111	50	50	0.1	2
NF112	50	50	0.2	2
NF113	50	50	0.05	2
NF121	50	50	0.1	0.5
NF131	50	50	0.1	0.1
NF211	20	50	0.1	2
NF311	10	50	0.1	2