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Relationship of relaxation property to reverse osmosis permeability in aromatic polyamide thin-film-composite membranes

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Abstract

We proposed a new approach to characterize the reverse osmosis (RO) permeability in conjunction with the macromolecular structures and inherent polymer properties for crosslinked and linear model aromatic polyamides. Aromatic polyamides were synthesized via interfacial reaction of phenylene diamines (*p*- and *m*-phenylene diamines) with either tri-functional (trimesoyl chloride) or di-functional (terephthaloyl and isophthaloyl chlorides) acyl halides.The relaxation properties obtained by cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectroscopy, in conjunction with the chemical structures, built a bridge between the specific polymer properties and the RO performance of the aromatic polyamides. The spin-lattice relaxation time in the rotating frame, $T_{1\rho}$ and hence chain mobility seemed to be an important parameter to control the RO membrane permeability. The longer $T_{1\rho}$ resulted from the crosslinked aromatic polyamides, in which presence of the crosslinking retarded local polymer motion, and a lower water flux resulted. In contrast, the shorter $T_{1\rho}$ for the linear crosslinked polyamides played a significant role for the higher water flux. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Thin-film composite membranes; Linear and crosslinked aromatic polyamides; Reverse osmosis permeability

1. Introduction

Reverse osmosis (RO) membrane separation plays an important role in commercial water treatment and water pollution control [1,2]. The current worldwide expansion and diverse application of the RO technology has resulted from the introduction of thin-film-composite (TFC) membranes and development of a numerous new polymeric materials for thin films of active layers [3–5]. Thin films perform as a perm-selective medium which allows the passage of solvent (water) and rejects the solutes. Most of the thin-film polymers in commercially successful TFC membranes are aromatic polyamides.

During the RO process the TFC membranes are treated essentially as a “black box”, and there have been a number of modeling approaches to understand transport properties and mechanisms through the membrane active layers [6–8]. It is recognized that most of the approaches originate from the viewpoints of chemical engineering, and there is an apparent lack of understanding of the active-layer polymers themselves which is of foremost and practical importance for fundamental RO engineering. As the performance and efficiency of the RO process primarily depend on the nature of the polymers forming the active layers, a new approach must be developed by establishing a correlation between the inherent chemical structure, the material behavior, and the RO transport characteristics in the TFC membranes.

Two essential membrane parameters in the RO process are solubility and diffusivity of solutes and solvents to the active-layer polymers [6–9], which determine the membrane rejection and the flux. The interrelationships between the RO membrane rejection and the polymer–solute/–solvent interactions, in conjunction with the chemical structure of the active-layer polymers, have been considerably studied [10,11]. In contrast, the effects of the inherent material properties of the active-layer polymers together with their chemical structure on the RO flux characteristics are rarely found in the literature. This is mainly ascribed to the characterization difficulties for the active-layer polymers; the active-layer polymers of most commercially successful TFC membranes are extremely thin and crosslinked, hence insoluble, thereby bringing about isolation difficulties and sampling problems for the characterization with conventional analytical techniques. A material property which may be useful for understanding membrane permeation and has a correlation with the RO flux is associated with the molecular relaxation and motion of the

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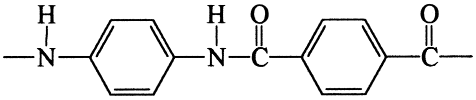
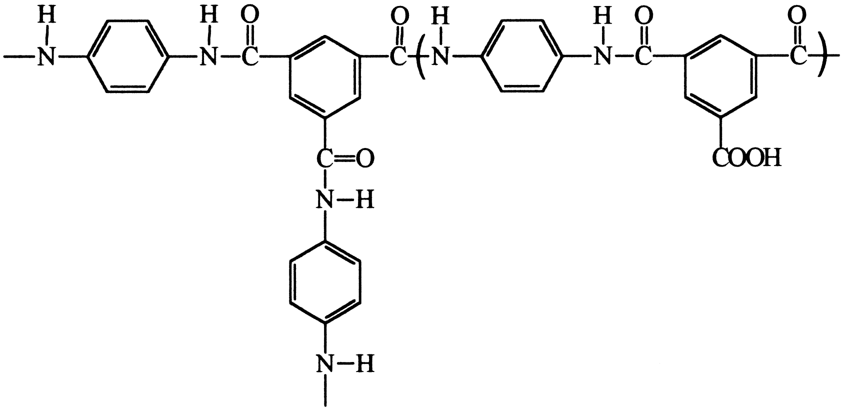
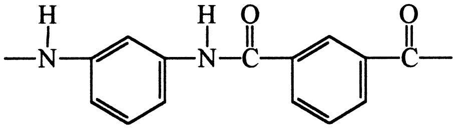
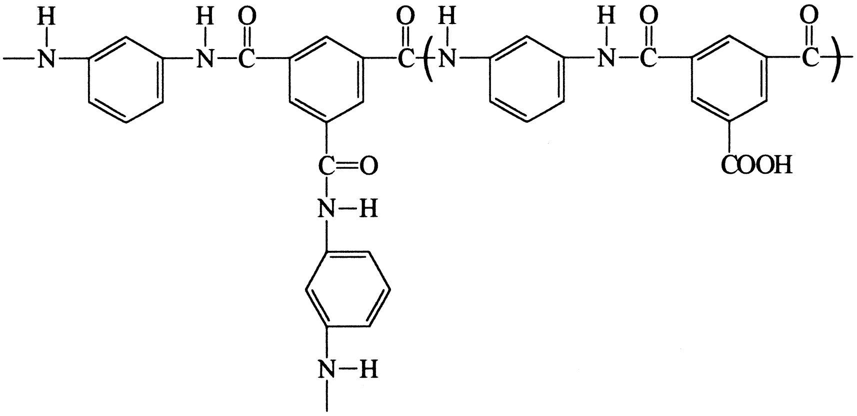
Table 1
Chemical structures of aromatic polyamides

	Chemical structure of repeat unit
PPD/TPC	
PPD/TMC	
MPD/IPC	
MPD/TMC	

active-layer polymers in their solid state. The chain mobility of the active-layer polymer must have some influence on the passage of the diffused-in solvent across the active layer, and becomes a dominant factor in governing the flux when the main driving forces of the RO process (i.e. pressure and concentration) are kept constant for the given membranes. Valuable information on the motion and relaxation can be provided by spin-lattice relaxation time in the rotating frame, $T_{1\rho}$ [12], as obtained by cross polarization/magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) experiments. The $T_{1\rho}$ spin-lattice relaxation times are considered to be a useful parameter to access the low motions in the kHz region, [13] and hence to explain RO membrane permeation.

In this study, two crosslinked and two linear aromatic polyamides were prepared via interfacial polymerization of phenylene diamines with either tri- or di-functional acid chlorides, and their chemical structure-relaxation

Table 2
RO characteristics of aromatic polyamides TFC membranes. (All the results were obtained with 3.5% synthetic seawater and at 1500 psi)

TFC membrane	RO characteristics			
	Water flux (gfd)		Salt rejection (%)	
PPD/TPC	53[a]	49[b]	38[a]	41[b]
PPD/TMC	7[c]	11[b]	99[c]	87[b]
MPD/IPC	—	56[b]	—	43[b]
MPD/TMC	17 ~ 25[d]	23[b]	99.2 ~ 99.5[d]	99.4[b]

[a] Ref. [15].
[b] Tested in the laboratory.
[c] Ref. [16].
[d] Ref. [17].

property-RO flux interrelationships were sought as a new approach to characterize transport characteristics of aromatic polyamide TFC membranes.

2. Experimental

2.1. Synthesis of aromatic polyamides

The diamines used in this study were 1,3-benzenediamine (*m*-phenylene diamine, MPD) and 1,4-benzenediamine (*p*-phenylene diamine, PPD). The acid chlorides were 1,3-benzenedicarbonyl chloride (isophthaloyl chloride, IPC), 1,4-benzenedicarbonyl chloride (terephthaloyl chloride, TPC), and 1,3,5-benzenetricarbonyl chloride (trimesoyl chloride, TMC).

Aqueous solutions (1.0% by weight) of the phenylene diamines were prepared using deionized distilled water (conductivity ~1.0 μmho). Organic solutions (1.0% by weight) of the acid chlorides were prepared in *n*-hexane. Aromatic polyamides were synthesized via interfacial polymerizations of the aqueous phenylene diamines with di-functional acid chlorides (i.e. IPC, TPC) and tri-functional acid chloride (i.e. TMC), which resulted in the linear and the crosslinked aromatic polyamides, respectively. The interfacial reaction process was accomplished without stirring and the fragments of the aromatic polyamide film formed at the solution interface were retrieved and precipitated in an excess of acetone. The solid polymer was then suction-filtered off, washed extensively with fresh water and methanol to remove the unreacted monomer remnants and occluded salt, and dried at 110°C in a vacuum oven. The final chemical structures of the resulting linear and crosslinked polyamides are believed to be as shown in Table 1.

2.2. Cross polarization/magic angle spinning ^{13}C NMR spectroscopy

The NMR experiments were performed with a Bruker MSL-200 spectrometer (4.7 T for ^{1}H) equipped with a MAS probe. The solid polymer samples were packed in the rotor and spun at the rate of about 3.5 kHz. A ^{1}H 90° pulse width of 4.5 μs was employed, and the repetition time for the net magnetization to be completely relaxed was 10 s. The proton spin-lattice relaxation times in the rotating frame, $T_{1\rho}$, were measured by analyzing the decay of specific carbon peak intensities after ^{1}H spin-lock-τ pulse sequence prior to the CP. The CP Hartmann–Hahn contact time was 1 ms.

2.3. Formation of thin-film-composite membranes and measurement of reverse osmosis performance

To fabricate the TFC membranes, support substrate composed of microporous polysulfone was first prepared in the laboratory by the following procedures. A solution of 18% (by weight) polysulfone (PSF; Udel P-7200, Amoco Co.) and 15% (by weight) polyvinylpyrrolidone (PVP; K-15, GAF Chemical Co.) in *n*-methyl-2-pyrrolidone (NMP; Aldrich Chemical) was cast onto a glass plate with a polyester nonwoven fabric using a 175 μm knife gap. The plate was immediately immersed in a water bath at room temperature in one smooth motion. Within 30 s, PSF gelled into a white microporous sheet; the top face (in contact with air) was used as a support surface for the TFC membrane. After a day, the PSF microporous support was removed, rinsed with water, and then stored in deionized water until its usage. Disks were cut from the PSF microporous support and saturated into aqueous solutions (1.0% by weight) of the individual phenylene diamines for 3 h. Excess of the diamine solution was squeezed off from the surface of the PSF support by means of a rubber roller fashioned from a length of glass tubing inserted through latex rubber tubing. The impregnated PSF substrate was then immediately covered with a solution of 1.0% by weight acid chloride in *n*-hexane for 2 min. This subjected an interfacial reaction as described earlier and a polymeric thin film was deposited upon the PSF support surface. The resulting TFC membrane was drained and air-dried at room temperature.

High-pressure RO tests were conducted, as described elsewhere [14], with an Akico RO apparatus (model FD01-100K-3). The apparatus was of a continuous flow type and consisted of a 20 l feed tank, three parallel stainless steel test cells (100 ml) with an effective membrane area of 20 cm^2, needle valves to control flow, and mechanical stirrers. Test conditions were 100 atm (1500 psi) feed-water pressure and the temperature of 25°C, and 3.5% by weight synthetic seawater (made with “sea-salt”, Han Joo Co., Korea). Membrane specimens were run under the test conditions for four days before 24-h collecting the permeate to characterize water flux and salt rejection. The water flux was determined by direct measurement of the permeate flow:

$$\text{flux (gfd)} = \text{permeate (gallon)}/\text{membrane area (ft}^2\text{)time (day)}.$$

The salt rejection rate was measured by the salt concentration in the permeate obtained through measurements of the electrical conductance of the permeate and the feed

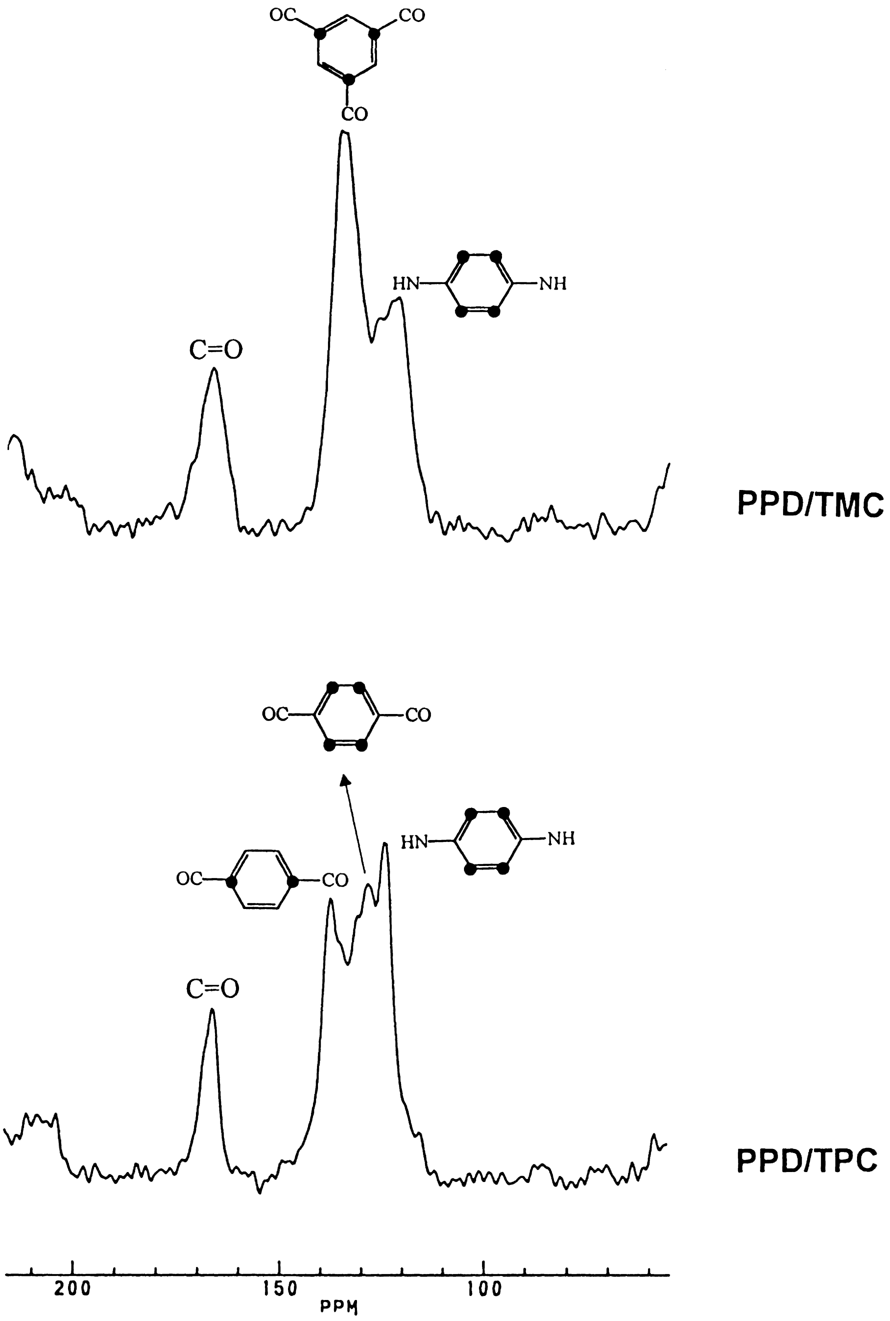


Fig. 1. ^{13}C high-resolution CP/MAS spectra of PPD/TPC and PPD/TMC polyamides.

using a conductance meter (YSI model 32):

$$\text{rejection }(\%) = (1 - \text{permeate conductance/feed conductance}) \times 100.$$

3. Results and discussion

Table 2 contains the RO performance data on the TFC membranes composed of the four aromatic polyamides. The data at the left of the water flux and salt rejection column were taken from the respective references [15–17] and those at the right were test results obtained in the laboratory. The linear aromatic polyamides (PPD/TPC, MPD/IPC) exhibit the water flux in excess of 50 gfd which is at least two times higher than that of the crosslinked aromatic polyamides (PPD/TMC, MPD/TMC). The salt rejections of the linear polyamides, however, are about a half or less of those of the crosslinked polyamides. The *meta*-positioned polyamides (MPD/IPC, MPD/TMC) are found to give a better water flux and salt rejection compared to *para*-positioned polyamides (PPD/TPC, PPD/TMC); this trend is more prominent in the crosslinked polyamides.

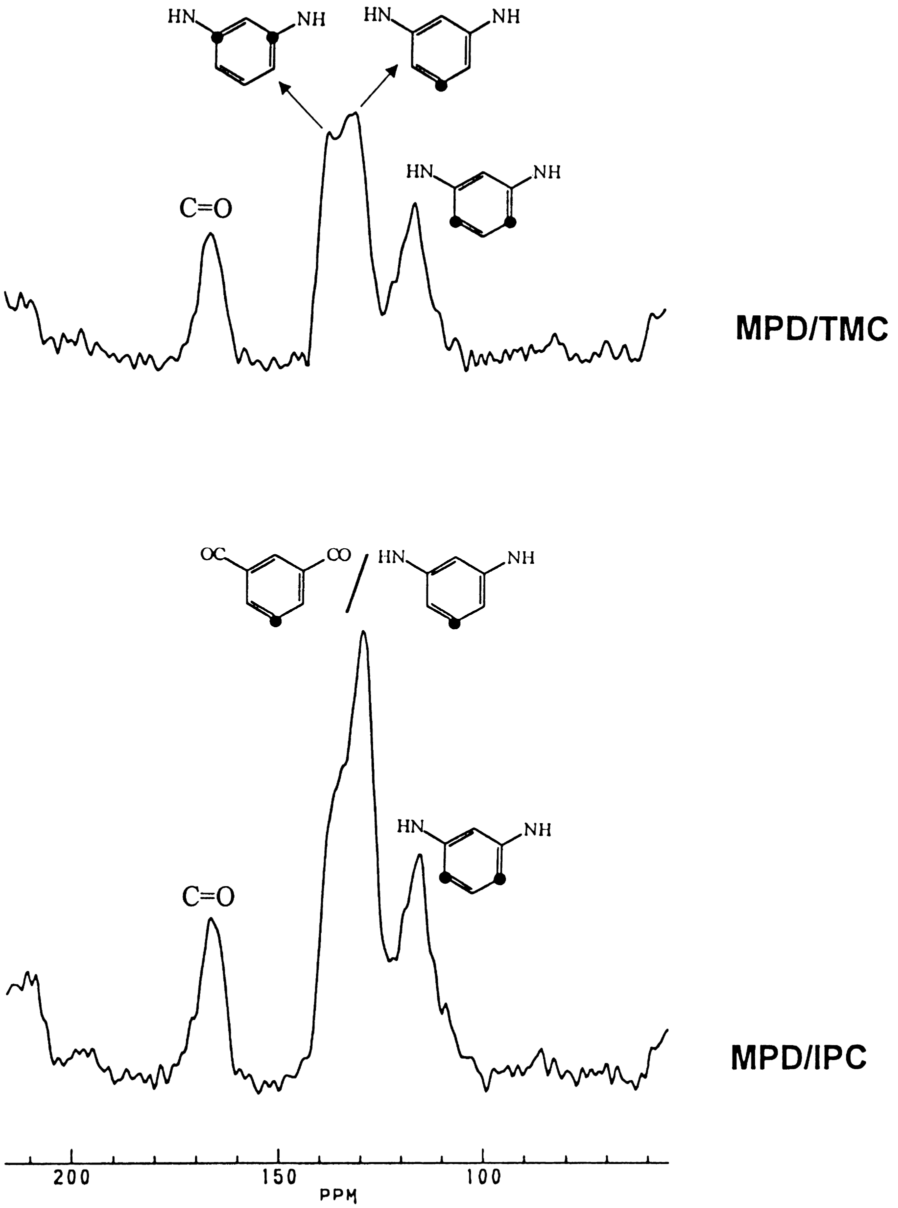


Fig. 2. ^{13}C high-resolution CP/MAS spectra of MPD/IPC and MPD/TMC polyamides.

The CP/MAS ^{13}C NMR spectra and peak assignments of the *para*-positioned polyamides and those of the *meta*-positioned polyamides are presented in Figs. 1 and 2, respectively. All spectra were taken using a CP contact time of 1 ms, which is long enough to allow for an effective magnetization transfer between hydrogen and most carbon spins. The peak assignments were performed by referring to the collection data on the chemical shifts of the various organic compounds [18]. Among the resonance carbons, the carbonyl carbons (C=O) and the protonated diamine aromatic carbons of the four aromatic polyamides were selected to measure the proton spin-lattice relaxation times in the rotating frame, $T_{1\rho}$. Variations in the resonance intensity, $M(\tau)$, for the specific carbons are obtained by the delayed-contact ^{13}C CP/MAS experiment where various delay times, τ, are inserted between the $\pi/2$ pulse and the spin-locking pulse. The resulting series of the ^{13}C spectra (namely, stack spectra) are shown in Fig. 3 for PPD/TMC. As the carbon magnetizations during the delay follow the decays in polarization of their proton reservoirs with a time constant equal to the $T_{1\rho}$ by such an exponential function,

$$M(\tau) = M_0 \exp(-\tau/T_{1\rho}) \qquad (1)$$

monitoring and analyzing of the resonance decays provide the $T_{1\rho}$ determination. Figs. 4–7 represent the plots of logarithmic $M(\tau)$ against τ for the crosslinked polyamides (PPD/TMC, MPD/TMC) and for the linear polyamides (PPD/TPC, MPD/IPC), respectively. The slopes of the straight lines yield the proton $T_{1\rho}$ relaxation times of the respective aromatic polyamides and the values are summarized in

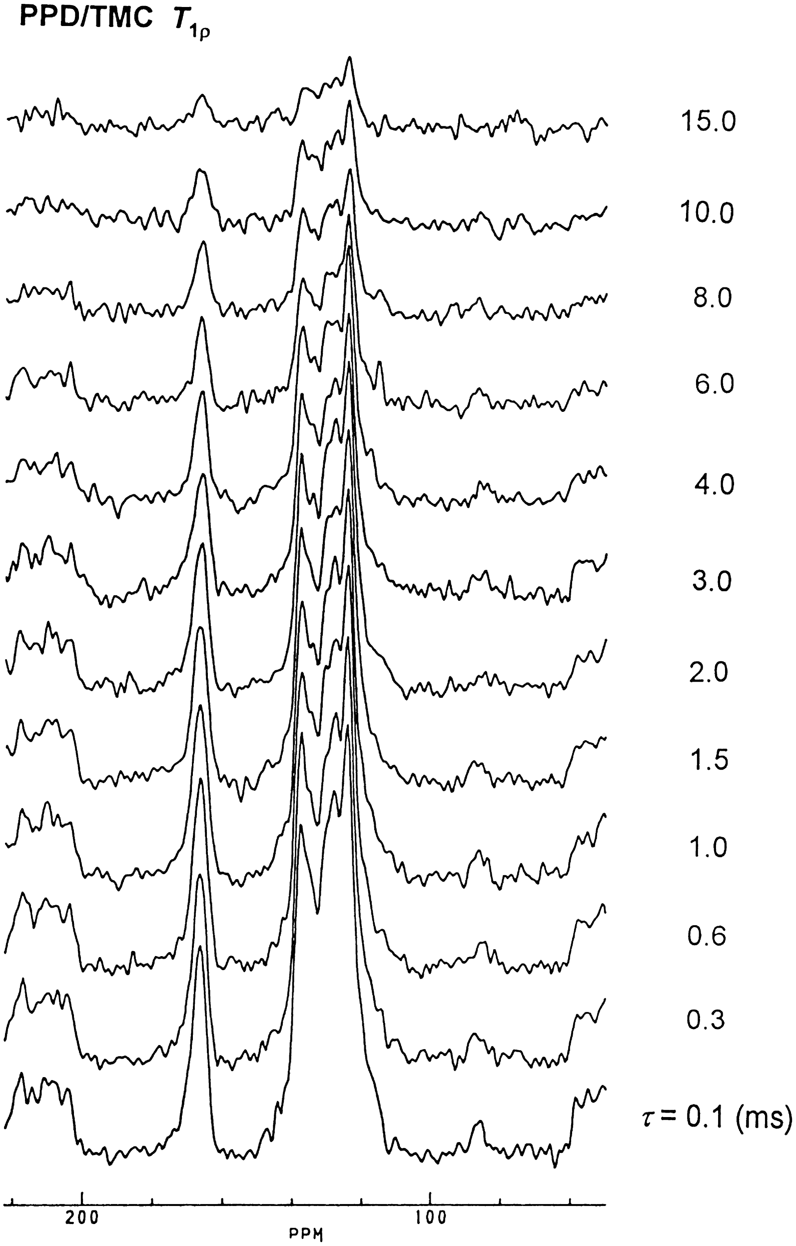


Fig. 3. $T_{1\rho}$ stack spectra of PPD/TMC polyamide.

Table 3. Single-component relaxation behavior is found in the specific carbons of all four aromatic polyamides, resulting in the respective single value of $T_{1\rho}$. As seen in Table 3, the $T_{1\rho}$ values of the aromatic polyamides become shorter in the order PPD/TMC, MPD/TMC, PPD/TPC, and MPD/IPC. In solid polymers, $T_{1\rho}$ is usually proportional to the correlation times, τ_c [19], which is understood to be the average time between molecular collisions:

$$1/T_{1\rho} \propto B_1^2\{\tau_c/(1 + 4\omega_1^2\tau_c^2)\}, \qquad (2)$$

where ω_1 is the resonance frequency (rad/s) in B_1 magnetic field. As τ_c defines the length of time that the molecule can be considered to be in a particular state of motion, the solid molecules with longer τ_c are in slower molecular motion and in general, $\tau_c^{rg} > \tau_c^{mb}$, hence $T_{1\rho}^{rg} > T_{1\rho}^{mb}$ follows [20], where the superscripts rg and mb relatively denote the rigid and mobile materials, respectively. Therefore, the ordering of $T_{1\rho}$ in Table 3 implies an increase of the mobility from PPD/TMC to MPD/IPC.

With reference to the RO date in Table 2, there is an obvious correlation of the $T_{1\rho}$ relaxation time with the RO permeation performance. The shorter the $T_{1\rho}$ relaxation time, the higher the water flux, and vice versa. Recognizing that the crosslinks in the polymer severely restrict the segmental mobility of the chains and the *para*-positioned polyamides are inherently far less flexible than all their *meta* isomers arising from axial symmetry, [21] the chain

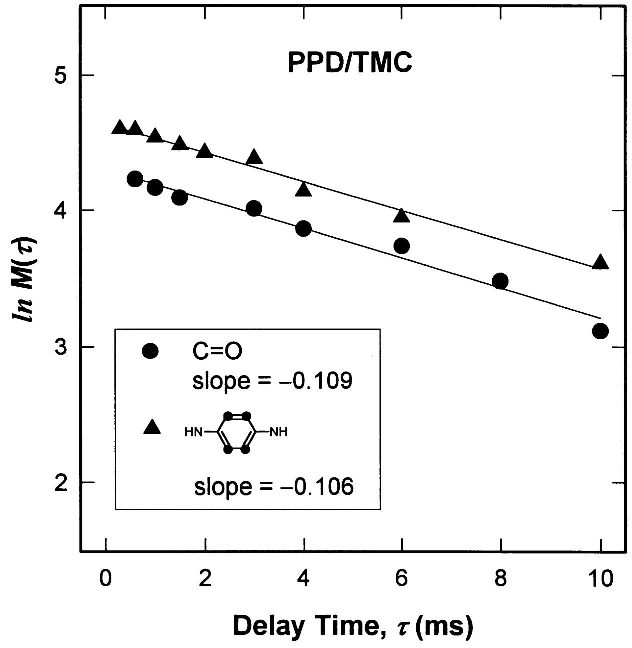


Fig. 4. Plot of $T_{1\rho}$ decay vs. various delay, τ, for PPD/TMC polyamide.

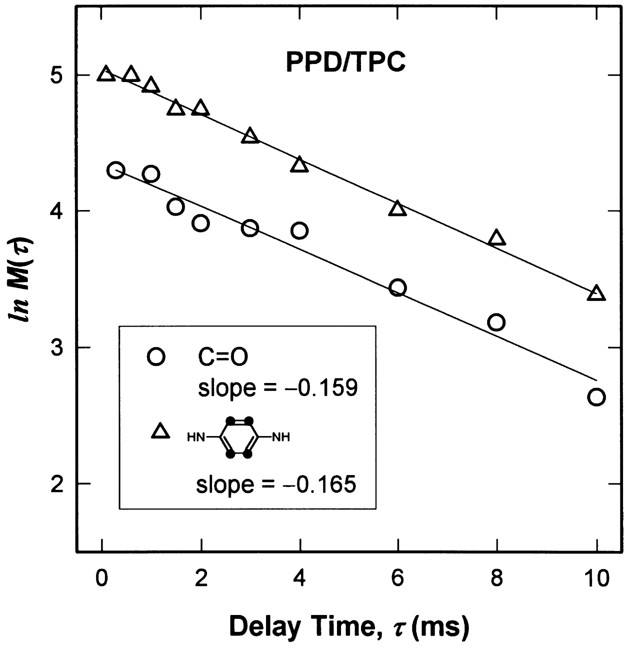


Fig. 6. Plot of $T_{1\rho}$ decay vs. various delay, τ, for PPD/TPC polyamide.

mobility might be MPD/IPC > PPD/TPC > MPD/TMC > PPD/TMC, which is in good agreement with the trend in the order of the $T_{1\rho}$'s in Table 3, i.e. $T_{1\rho}^{\mathrm{MPD/IPC}} > T_{1\rho}^{\mathrm{PPD/TPC}} > T_{1\rho}^{\mathrm{MPD/TMC}} > T_{1\rho}^{\mathrm{PPD/TMC}}$.

4. Conclusions

A structural and relaxational understanding of the macroscopic processes responsible for the RO permeation of the aromatic polyamides demonstrated the ability to probe transport characteristics from the material viewpoint. This approach would further offer a strong potential for designing and manufacturing the new TFC membranes with maximum performance.

The RO experiments demonstrated that MPD/IPC, PPD/TPC, MPD/TMC, and PPD/TMC were in the order of higher to lower permeation. The water flux of the linear polyamides (MPD/IPC, PPD/TPC) was shown to be at least twofold higher than that of the crosslinked ones; the salt rejection

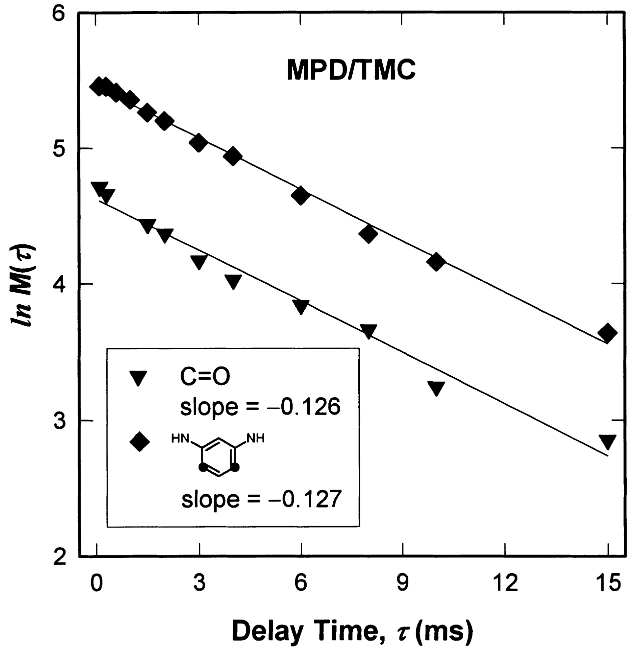


Fig. 5. Plot of $T_{1\rho}$ decay vs. various delay, τ, for MPD/TMC polyamide.

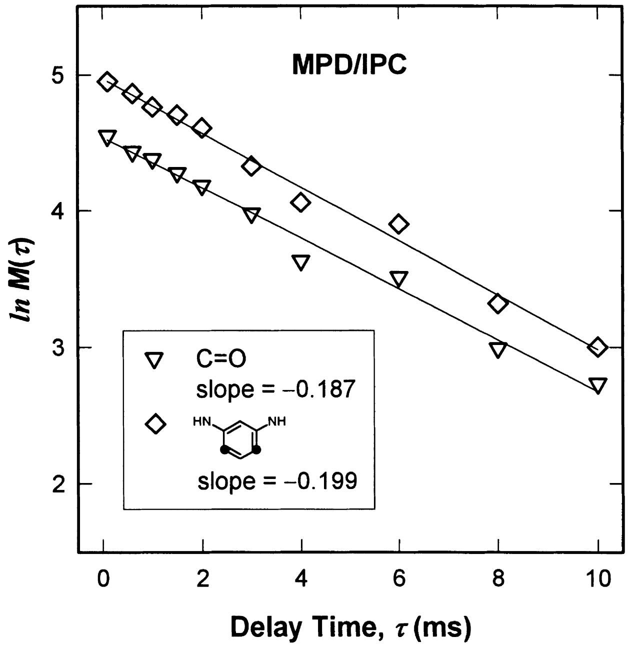
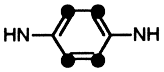
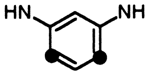
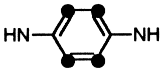
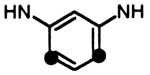


Fig. 7. Plot of $T_{1\rho}$ decay vs. various delay, τ, for MPD/IPC polyamide.

Table 3
$T_{1\rho}$ relaxation times of aromatic polyamides

Aromatic polyamide	Peak position	$T_{1\rho}$ (ms)	Peak position	$T_{1\rho}$ (ms)
PPD/TMC	C=O	9.17		9.43
MPD/TMC	C=O	7.94		7.87
PPD/TPC	C=O	6.29		6.06
MPD/IPC	C=O	5.35		5.03

reversed the trend. The *meta*-positioned polyamides (MPD/IPC, MPD/TMC) were found to give a higher water flux and salt rejection than their *para*-positioned isomers (PPD/TPC, PPD/TMC).

The CP/MAS ^{13}C NMR spectroscopy, measuring the proton spin-lattice relaxation times in the rotating frame ($T_{1\rho}$), provided information on the degree of molecular motion for the aromatic polyamides. On the basis of the determination of the $T_{1\rho}$ relaxation times, in conjunction with the chemical structure of polyamides, the mobility was found to play a significant role in governing the RO permeability of the polyamides. Symmetrical molecules of *para*-based polyamides and introducing crosslinks froze the local polymer motion, which resulted in the longer $T_{1\rho}$ relaxation times. This reflected active layers with less mobile chains and in turn retarded water diffusion. Combined results of the RO performance tests and CP/MAS ^{13}C NMR relaxation measurements concluded that the material properties of the shorter $T_{1\rho}$ relaxation time were favorable for the membranes with higher water flux, and vice versa.

Acknowledgement

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