Investigation of the Viscoelastic and Transport Properties of Interfacially Polymerized Barrier Layers Using Pendant Drop Mechanical Analysis

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ABSTRACT: Pendant drop mechanical analysis (PDMA) enables the mechanical and transport characterization of unsupported interfacially polymerized (IP) thin films. PDMA was used to study the viscoelastic and permeation behavior of films formed by the interfacial polymerization of *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC). The viscoelastic properties were obtained by stress-relaxation experiments wherein IP films on the surface of aqueous MPD drops were deformed and the decrease in the internal pressure resulting from stress relaxation was monitored with time. The stress-relaxation behavior was interpreted using the fractional exponential relaxation model. The two model parameters, τ and β, are related to the degrees of crosslinking and branching, respectively. Water transport was generated by an osmotic gradient across the IP films, and permeation data were obtained by monitoring the increase in the drop size with time. Whereas the network structure was relatively insensitive to MPD concentration, the TMC concentration had a significant effect on the degrees of crosslinking and branching; τ evidenced a maximum at 0.1 wt % TMC concentration and β decreased monotonically with TMC concentration. The effect of organic-phase reactant functionality was studied by incorporating isophthaloyl chloride (difunctional) with TMC. For TMC fractions > 25 wt %, the network structure was relatively insensitive to TMC fraction in the isophthaloyl chloride–TMC mixture. The transport experiments enabled the determination of a membrane constant A. The transport results generally corroborated the trends observed in the stress-relaxation experiments, thus demonstrating the close association between the network structure and transport behavior. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 558–568, 2004

Key words: membranes; polyamides; mechanical properties; pendant-drop mechanical analysis (PDMA); interfacial polymerization

INTRODUCTION

The FT-30 class of thin film composite (TFC) membranes is widely used in desalination and other water-treatment applications. The ultrathin barrier layer ($\sim$ 0.1–0.25 μm) of these membranes is formed from the interfacial polymerization (IP) of *m*-phenylenediamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase (hexane or freon).[1] When the two phases are brought into contact, MPD from the aqueous phase reacts with TMC to produce an insoluble crosslinked film (the barrier layer) at the interface. The film formation immediately retards and eventually inhibits the interfacial reaction. The IP reaction for the MPD–TMC system is generally considered to be instantaneous.[1–3] Barrier-layer formation by IP has several important advantages including minimal thickness for high flux, the lack of strict requirements for reactant purity and stoichiometry, and the avoidance of film defects such as macrovoids.

Many studies have been conducted on the IP formation process in the FT-30 as well as other appropriate systems. A recent review of the literature[4] indicates that most work has focused on assessing the effects of various chemical parameters, such as the reactant functionality and type, on IP-TFC performance. In contrast, studies by Arthur[5] and Jiang and coworkers[6] suggest that membrane transport depends on the extent of free volume and the conformational mobility of the polymer chains. Thus, TFC performance should be closely related to the barrier-layer network structure. Interestingly, very little subsequent information in the open literature specifically addresses the relationship between the barrier-layer network structure and thin film performance. This situation may reflect the inherent complexities of the IP film-formation process. For example, the nearly instantaneous nature of the IP process precludes the application of many real-time characterization techniques. In addition, because the IP film is crosslinked

and thus insoluble in most common solvents, conventional spectroscopic techniques cannot be easily used. Moreover, standard mechanical characterization is difficult to apply to ultrathin films.

In response to these limitations, our research group developed pendant drop mechanical analysis (PDMA), which exploits the capabilities of a specially modified pendant drop tensiometer. By monitoring the pressure and deformation responses of an IP film formed at the surface of a liquid drop, the viscoelastic and transport properties of the unsupported barrier layer can be obtained.[4,7,8] Whereas a previous study[4] focused only on the effect of TMC concentration on film behavior, this article describes the results of a series of systematic PDMA experiments that consider the effect of reactant composition and contact time as well as organic-phase functionality on unsupported barrier layers formed from the MPD–TMC system by IP. This study provides valuable insights regarding the evolution of the network structure, the dependency of the network structure on the film-formation parameters, and the relationship between structure and transport performance.

This article is organized as follows. Because PDMA viscoelastic characterization was achieved through stress-relaxation experiments, the next section includes a brief description of the fractional exponential relaxation model that was used to interpret the stress-relaxation data; this same section also discusses the likely mechanisms of stress-relaxation in the IP thin films and the physical significance of the parameters of the fractional exponential relaxation model. The experimental section includes details as well as the protocols used in conducting the stress relaxation and transport experiments by PDMA. The results and discussion section includes the PDMA results and discusses the implications of these results on our understanding of the network structure and the relationship between structure and transport performance. The final section summarizes the key insights obtained through this study.

STRESS RELAXATION CHARACTERIZATION OF IP FILMS BY PDMA

As indicated in the literature, the fractional exponential relaxation model has often been used to describe various relaxation phenomena in different polymers.[9–14] Indeed, this model was used to analyze stress-relaxation data obtained by PDMA.[4] The fractional exponential relaxation model is empirical in nature, and contains two "fitting" parameters τ and β:

$$\sigma(t) = \sigma_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta} \right] \qquad (1)$$

where $\sigma(t)$ and σ_0 are the instantaneous and the initial stresses, respectively. Assuming that the IP film thickness change is negligible during stress relaxation, the above equation can be rewritten in terms of the instantaneous [$p(t)$] and initial IP-drop internal pressure (p_0), as follows:

$$\frac{p(t)}{p_0} = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta} \right] \qquad (2)$$

The stress relaxations described by the fractional exponential relaxation model are controlled by continuous relaxation spectra, and the relaxation spectrum $\varphi(t)$ can be analytically expressed as[15]

$$\varphi(t) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!\Gamma(-\beta n)}\left(\frac{t}{\tau}\right)^{\beta n} \qquad (3)$$

Figure 1(a) illustrates the effect of β on the relaxation spectrum, wherein $\varphi(t)$ is plotted versus time for the same characteristic relaxation time τ (1000 s), but for different values of β. For the higher value ($\beta = 0.411$), the peak is much narrower, compared to that for the lower value ($\beta = 0.211$). The parameter β is thus closely related to the breadth of the spectrum (i.e., for higher values of β, the distribution peak becomes narrower and more intense). The characteristic relaxation time τ indicates the position of the peak in the relaxation spectrum such that larger values of τ correspond to a shift in the peak to longer times [Fig. 1(b)].

Although the fractional exponential relaxation model can provide a good fit to experimental relaxation data, establishing a general physical significance for the empirical parameters τ and β is difficult.[16] This limitation occurs because a combination of different factors including the molecular weight distribution, the presence and the weight distribution of crosslinks, the crosslink polyfunctionality, and the presence of entanglements could all lead to similar values of τ and β. Thus, to obtain useful insights from the PDMA stress-relaxation experiments, we must consider the likely characteristics of the IP films formed from the MPD/TMC system.

The interfacial reaction between MPD and TMC is shown in Figure 2. Because TMC is trifunctional, linear chain propagation and branching occur simultaneously. Crosslinking occurs when the acid chloride group of an available branch reacts with an amine group of another linear chain. Hydrolysis of the unreacted acid chloride groups gradually occurs and gives the IP film a mildly acidic character.[2] The hydrolyzed groups substantially affect the flux properties of the final TFC membrane. A key feature of the IP process is that linear chain formation, branching, and crosslinking occur simultaneously. In addition, the extent of unreacted acid chloride groups (which later hydrolyze) depends on the degree of branching and crosslinking. Given these characteristics, the resulting
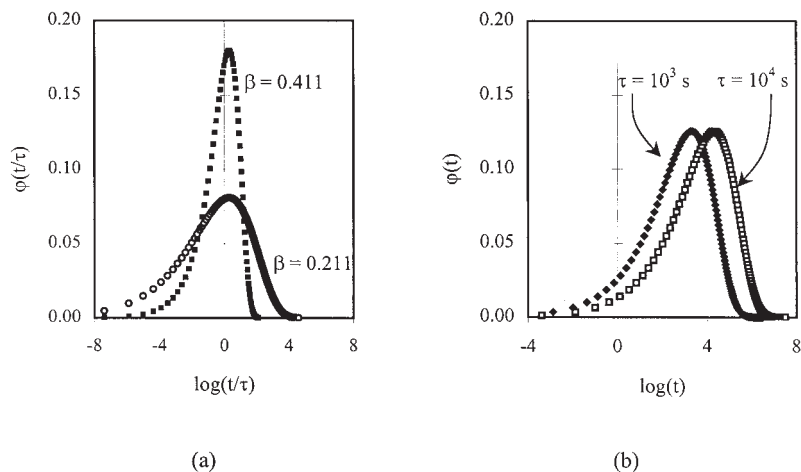
Figure 1 Typical relaxation spectra obtained by using the fractional exponential relaxation model. (a) The effect of β on the relaxation spectrum. The distribution peak is narrower with a greater intensity for larger values of β. Also, note that the maximum in the spectrum occurs at a time slightly greater than τ [eq. (3)]. (b) The effect of τ whereby the distribution peak occurs at longer times for larger τ values.

IP polyamide should be fundamentally different from those network polymers in which crosslinks are introduced between linear chains (for example, by irradiation) subsequent to linear chain formation.

Aharoni et al.[17–19] studied systems involving multifunctional monomers that yield crosslinked polyamides through *in situ* condensation reactions. They proposed that in the *in situ* polyamidation reactions, a relatively small number of highly branched, high molecular weight macromolecules are formed, and the reaction mixture contains a changing distribution of lower molecular weight macromolecules, extending down to monomeric size. The molecular weight and the molecular weight distribution of the macromolecules change during the condensation reaction, resulting in a polymeric network encompassing the whole reaction volume within which other macromolecules of lower molecular weight interpenetrate and nestle in voids and irregular surfaces. According to Aharoni et al., the initiation of the structure is through the formation of random nuclei that form polymer fractals. These fractals cluster together, and when a sufficient number of them grow large, a contiguous network i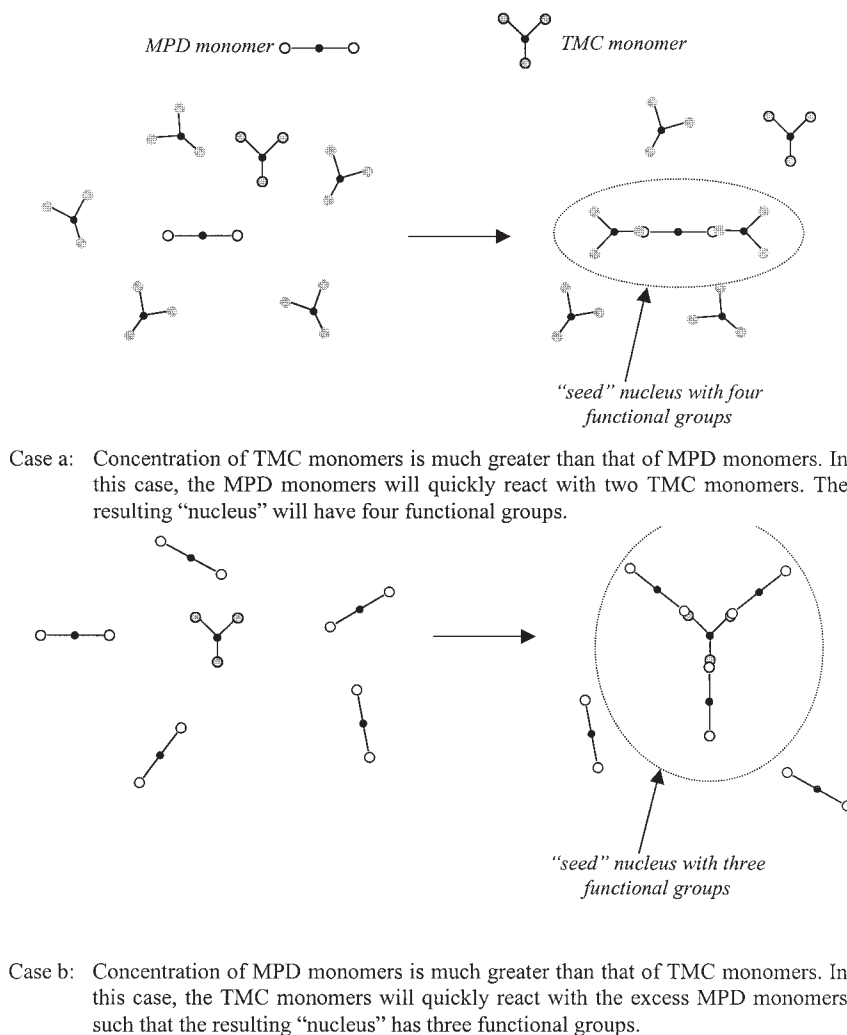s formed. Such networks, which they termed "fractal polymers," are intrinsically different from conventional crosslinked networks, in which crosslinks are introduced between linear chains.

Clearly, the conditions of IP film formation in the MPD–TMC system are somewhat different from those studied by Aharoni et al. In particular, IP film formation occurs only at the interface rather than in the bulk. Also, the addition of MPD and TMC monomers occurs at opposite ends of the interface. However, these differences should not alter the essential mechanism of network formation. Thus, even in the MPD–TMC system, the resulting IP film most likely evidences a broad spectrum of molecular weights.

Because the IP network formation occurs by a nucleation and growth mechanism, the network characteristics would be determined by the instantaneous TMC and MPD concentrations at the reaction front. These in turn depend on the magnitude of the TMC and MPD fluxes. Thus, for the MPD–TMC system, two factors, the ratio and the magnitude of the instantaneous monomer fluxes to the reaction front, should play a pivotal role in determining the structure of the eventual network. For example, if the flux of the TMC monomers is much greater than that of the MPD monomers, then individual MPD
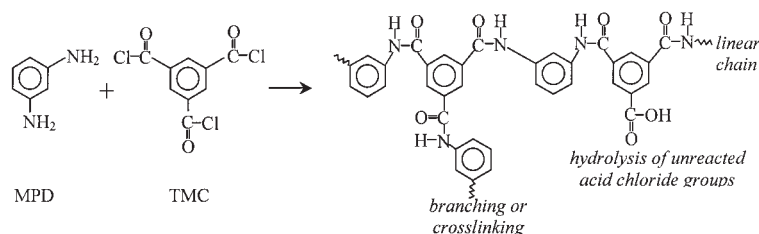
Figure 2 MPD–TMC reaction showing simultaneous branching, crosslinking, and linear chain formation. The unreacted acid chloride groups gradually hydrolyze so that the membrane has a mildly acidic character.

Case a: Concentration of TMC monomers is much greater than that of MPD monomers. In this case, the MPD monomers will quickly react with two TMC monomers. The resulting "nucleus" will have four functional groups.

Case b: Concentration of MPD monomers is much greater than that of TMC monomers. In this case, the TMC monomers will quickly react with the excess MPD monomers such that the resulting "nucleus" has three functional groups.

Figure 3 Schematic of IP network evolution. The crosslinking/branching characteristics depend on the relative concentrations of TMC and MPD monomers in a given region.

monomers will be surrounded by the TMC monomers, thereby forming a "seed" nucleus having four functional groups. This is schematically shown in Figure 3. In contrast, if the instantaneous flux of the MPD monomers is much greater, then the individual TMC monomers will be surrounded by the MPD monomers and the seed nucleus would have three functional groups (Fig. 3). Although the monomer flux ratio determines the fractal dimensionality, the monomer flux magnitude would determine the number density of the nuclei. Very low monomer fluxes would result in relatively fewer nuclei in a given volume. Their fractal growth would occur to a greater extent before they begin to interact with each other. In contrast, when the fluxes are higher, a greater number of nuclei will be formed, and interactions between the nuclei will occur before a similar extent of fractal growth occurs. The continuous network formed under the latter conditions would be restricted and have greater degrees of crosslinking compared to those of the former. The exact relationship between the crosslink

density and the monomer concentrations is thus complex.

If the IP polyamide network has a wide distribution in the molecular weights of the linear as well as of any pendant chains, a distribution in the relaxation time spectrum is expected, given that each of the chains/branches has a different characteristic relaxation time. Now, the characteristic relaxation time τ is generally associated with the structural rigidity.[15,20] In this specific context, τ can indicate the relative degree of crosslinking. Likewise, because β is related to the broadness of the relaxation-time spectrum,[15] β may reflect the polydispersity of the linear chain segments as well as the degree of branching.

EXPERIMENTAL

Materials

Analytical-grade MPD was obtained from Aldrich (Milwaukee, WI) and stored in a dark, dry environ-
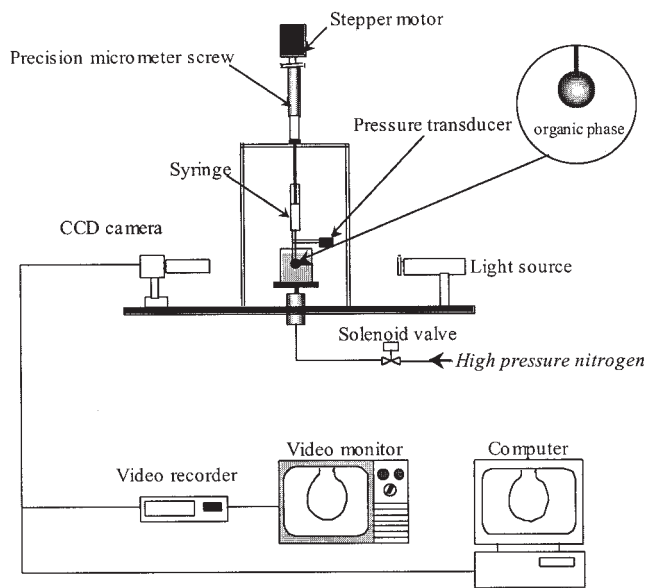
Figure 4 Schematic of the PDMA apparatus. The IP film is formed on the surface of a drop that is approximately 2 mm in diameter. A stepper motor attached to a precision micrometer screw enables the injection of liquid into the drop at controlled rates.

ment; analytical-grade TMC was obtained from Sigma Chemicals (Milwaukee, WI) and stored in a desiccator at −4°C. TMC is hygroscopic and, when kept on the shelf for a long time, can hydrolyze in the presence of atmospheric moisture. Whereas pure TMC is crystalline and readily soluble in heptane, hydrolyzed TMC is amorphous and leaves an insoluble residue when mixed with heptane. Hence, TMC was used only as long as no residue was observed during mixing with heptane. Analytical-grade isophthaloyl chloride (IPC; Sigma Chemicals) was stored in exactly the same manner as TMC. Analytical-grade heptane, used as the organic-phase solvent, was obtained from Fisher Scientific (Hampton, NH). Analytical-grade sodium chloride, obtained from Fisher Scientific, was used in the PDMA transport experiments. All materials were used as received without additional processing. In all experiments, distilled and deionized water was used whenever required.

PDMA methodology

Because the protocol for conducting PDMA experiments was recently explained in detail,[4] only brief descriptions of the apparatus and experimental methodology are included here. The PDMA technique is based on the principles of pendant-drop tensiometry; a schematic of the apparatus is shown in Figure 4. The IP reaction occurs when a drop of the aqueous phase containing MPD suspended at the tip of a syringe is brought into contact with a surrounding organic

phase containing TMC so that an IP film forms on the surface of the drop. The initial size of the drop is typically about 2 mm in diameter. Rapid contact between the two phases is achieved when a platform supporting a beaker of the organic phase is raised pneumatically by the activation of a solenoid valve that allows high-pressure nitrogen gas to flow to the platform to provide nearly instantaneous lift.

In stress-relaxation experiments, a predetermined amount of liquid from the syringe is injected into the drop at a controlled rate of 0.3 μL/s after an IP film has formed on the drop surface. Because the drop volume and surface area increase, deformation of the IP film and an increase in the internal pressure of the drop occur. Upon cessation of liquid injection, the drop volume remains constant and the drop internal pressure decreases with time because of stress relaxation within the IP film. The pressure-drop/time profiles are recorded over a time period of 20 min and provide information about the IP film network structure. It is important to note that the time scale of the relaxation experiments was short enough to ensure that the assumption of constant volume was valid but long enough to observe differences in behavior.[4]

The transport experiments conducted in this study are unique in that the obtained response was attributed only to the barrier layer, with no contribution from a support layer. Solvent (water) transport occurred because of an osmotic gradient across the barrier layer, which was achieved by adding a small quantity of NaCl to the aqueous MPD solution. Upon subsequent IP reaction and barrier-layer formation, the drop was immersed in a large quantity of deionized and distilled water, whereupon water was transported into the drop due to the result of osmotic gradient. Permeation data were obtained by monitoring the increase in the drop size with time using a CCD camera; the permeation properties were reported in terms of the membrane constant A. The details of the mathematical model used to obtain A were described previously.[4] A is a lumped parameter that incorporates the effects of the permeability of the membrane (a material parameter) and the film thickness (a geometric parameter). Larger values of A imply a greater capability for solvent (water) permeation through the membrane.

Experimental design

The parameters chosen for this study were MPD concentration, TMC concentration, organic-phase functionality (TMC/IPC mass ratio), and contact time. The MPD and TMC concentrations were varied between 0.1 and 4 wt % and 0.005 and 0.8 wt %, respectively. Three contact times, 20 s, 1 min, and 5 min, were studied. The functionality of the organic-phase reactant was varied using mixtures of TMC and IPC. IPC

is a difunctional acid chloride, whereby a reaction between MPD and IPC results in the formation of linear chains only. Two main sets of experiments were performed: stress relaxation and water transport. Four replications, at a minimum, were used for each condition corresponding to the stress-relaxation experiments, and at least three replications were used for each condition corresponding to the much longer transport experiments. Statistical significance of the results was determined using standard statistical methodology, that is, a one-way analysis of variance (ANOVA) followed by a Tukey test to identify the levels that were statistically different.[21]

RESULTS AND DISCUSSION

Stress-relaxation experiments

Effect of TMC concentration

The TMC concentration was varied over a wide range, from 0.005 to 0.8 wt %. In these experiments the MPD concentration was held constant at 2 wt %, and three contact times (20 s, 1 min, and 5 min) were tested. The lowest TMC concentration (0.005 wt %) resulted in extremely fragile films at all three contact times. These fragile films could not withstand the small deformation that was necessary for the stress-relaxation experiments. The effect of TMC concentration on film behavior is summarized in Figure 5, where for each of the three contact times, plots (a), (c), and (e) and plots (b), (d), and (f) indicate the behavior of τ and β, respectively. Statistical analysis indicated that differences among the τ and β values at each contact time are highly significant ($p < 0.001$ for τ and $p < 0.005$ for β). For all three contact times, τ attained a maximum value at 0.1 wt % TMC concentration, whereas to a first approximation, β decreased monotonically from 0.3 to 0.2 with increasing TMC concentration.

The results obtained for τ suggest that the degree of crosslinking reaches a maximum at an intermediate TMC concentration of 0.1 wt %. Interestingly, this same concentration apparently yields optimum permeation properties for flat-sheet FT-30 systems.[22] Based on the description of the IP process provided earlier, a correspondence between the structural characteristics of the IP film and membrane performance would be reasonable to the extent that the barrier layer accounts for the permselective properties of the membrane.

Because the values of β most likely reflect the degree of branching, as discussed earlier, the β response is consistent with a systematic increase in the degree of branching with an increase in the initial TMC concentration. The relatively low τ and high β values at low TMC concentrations thus result in the formation of a less-extensive network structure. As the TMC concentration increases, the degree of crosslinking as

well as branching increases. Initially, crosslinking predominates, as reflected in the maximum in τ at 0.1 wt % TMC, whereas at higher TMC concentrations, branching predominates over crosslinking, causing both τ and β to decrease.
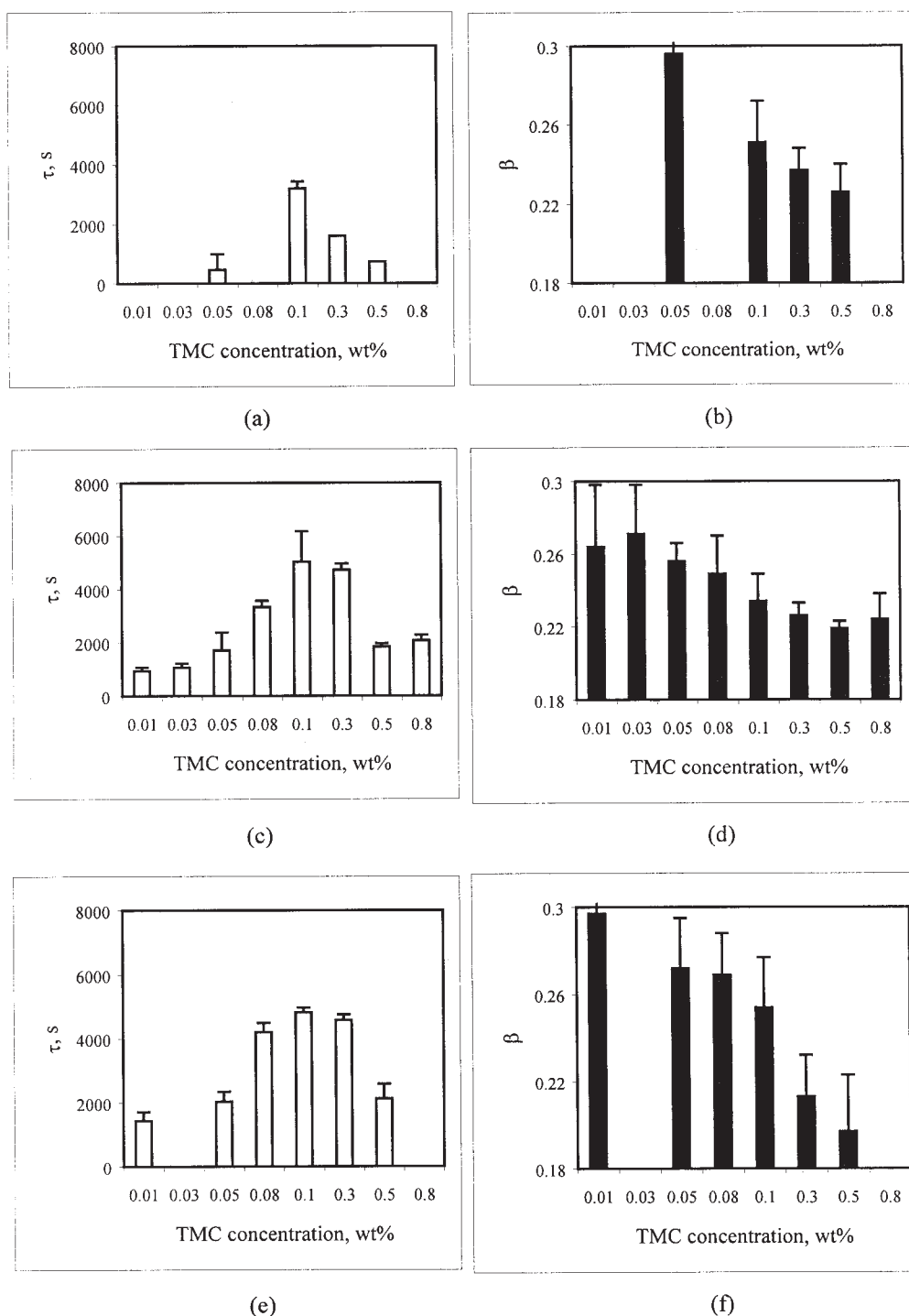
Effect of MPD concentration

For these stress-relaxation experiments, the TMC concentration and the contact time were held constant at 0.1 wt % and 1 min, respectively, whereas the MPD concentration was varied over the range 0.1–4 wt %. Results from these experiments are presented in Figure 6; again, statistical analysis indicated that the differences among τ and β values are highly significant ($p < 0.001$). Values of τ are initially low at 0.1 wt % MPD but increase from 1000 to 5000 s as the MPD concentration increases to 1 wt %. For higher MPD concentrations τ remains essentially constant [Fig. 6(a)]. The general characteristics of the change in β with MPD concentration are quite similar [Fig. 6(b)]. Overall, the low τ and β values at low MPD concentration suggest the formation of a network with a relatively lower degree of crosslinking but more pronounced branching. However, in the range of MPD concentrations typically used for commercial FT-30 membrane fabrication (1–4 wt %),[22] the degree of crosslinking is higher and remains relatively constant.

Effect of organic-phase reactant functionality

The functionality of the organic-phase reactant was systematically varied by using different proportions (by weight) of IPC (difunctional) and TMC (trifunctional) monomers in heptane. The TMC proportion was varied from 0 to 100%, whereas the MPD concentration was maintained at 2 wt %. The experiments were conducted at two different total acid chloride concentrations (by weight): 0.1 and 0.5 wt %. The IP films formed using 100% IPC were too fragile to be characterized by stress relaxation.

The effect of functionality on the stress-relaxation parameters τ and β is shown in Figure 7 as a function of total acid chloride concentration. The results [Fig. 7(a)] indicate that τ increases by about 12% as the TMC concentration increases from 25 to 50 wt %. However, statistical analysis indicated no significant differences among the τ values. In addition, statistical analysis of the β data [Fig. 7(b)] indicated no significant differences attributed to the composition variation in the organic-phase reactants. Although different combinations of crosslinking/branching could result in structures with similar values of τ and β, it seems unlikely that this would occur as the proportion of TMC was increased over such a large range (25 to 100%). A more reasonable explanation is that the macroscopic behavior of the film is relatively insensitive to the organic-
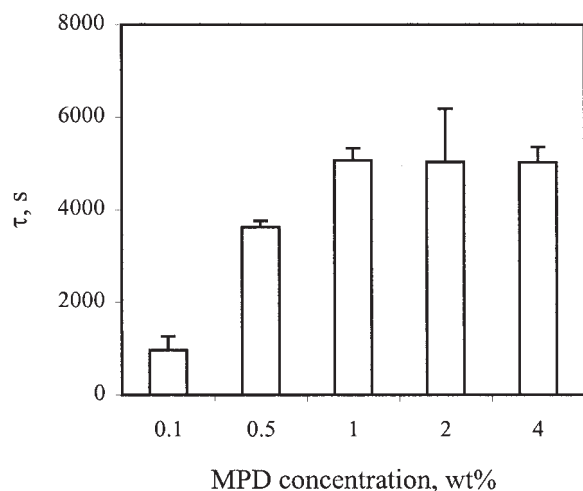
Figure 5 Effect of TMC concentration on values of τ and β. The contact times tested were 20 s (a and b), 1 min (c and d), and 5 min (e and f). For all the contact times, τ attained a maximum at 0.1 wt % TMC concentration, whereas β decreased monotonically. For each of these experiments, the MPD concentration was held constant at 2 wt %.

phase reactant functionality as long as the crosslinking monomer (TMC) is present in sufficient proportion.

Comparison of the results presented in Figure 5(c) with those in Figure 7(a) indicates that for lower total acid chloride concentrations (0.1 wt %), τ is significantly increased in the presence of IPC relative to the same concentration of TMC in the nonmixed formu-

lation. For example, the τ value for the IP films formed from a 50/50 wt % TMC/IPC mixture is 4680 ± 530 s [Fig. 7(a)]. In these film-forming conditions, the TMC concentration was 0.05 wt %. However, the τ value for the IP films formed using a 0.05 wt % pure TMC solution was much smaller [i.e., 1700 ± 680 s; Fig. 5(c)]. For the higher levels of total acid chloride con-
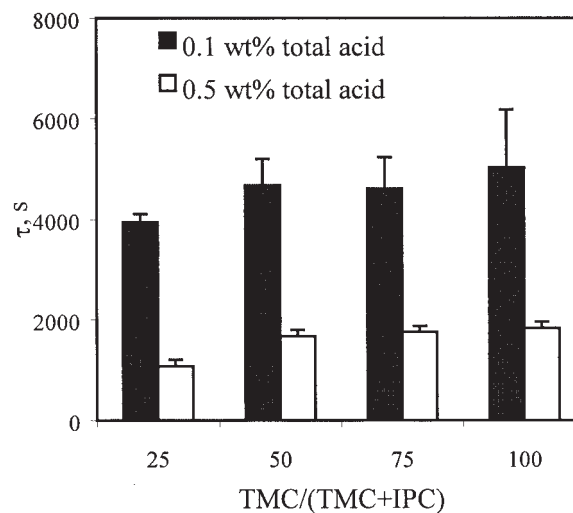
(a)
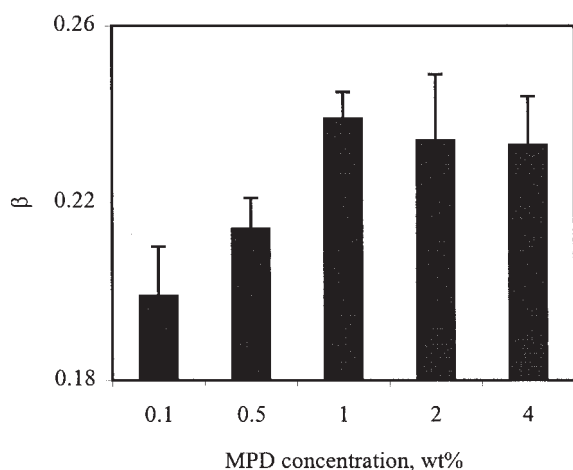
(b)

Figure 6 Effect of the MPD concentration on values of τ and β. For these experiments, the TMC concentration and the contact time were held constant at 0.1 wt % and 1 min, respectively.

centration (0.5 wt %), the opposite effect is observed, whereby τ is significantly decreased in the presence of IPC. The reason for this behavior is not clear. Because similar values of τ may be obtained for rather different chain structures to which crosslinking, branching, and molecular weight effects all contribute to varying degrees, the effect of IPC may reflect a structural continuum, which might result from concentration-dependent monomer reactivity differences.

Effect of contact time

The effect of contact time is shown in Figure 8 for TMC concentrations of 0.1 and 0.5 wt %. The results indicate

that an increase in the contact time from 20 to 60 s leads to a statistically significant increase in τ for each composition. However, no statistically significant changes in τ are observed when the contact time is increased from 1 to 5 min. Because of the relatively larger variability in the β values, no statistically significant trends regarding the effect of contact time can be identified. Overall, the data suggest that in the PDMA configuration, at least 60 s are required for the completion of the IP process. In contrast, many earlier references in the IP literature cite very rapid reaction
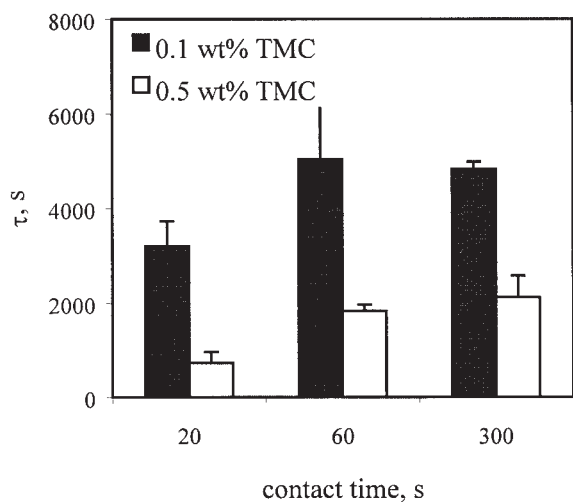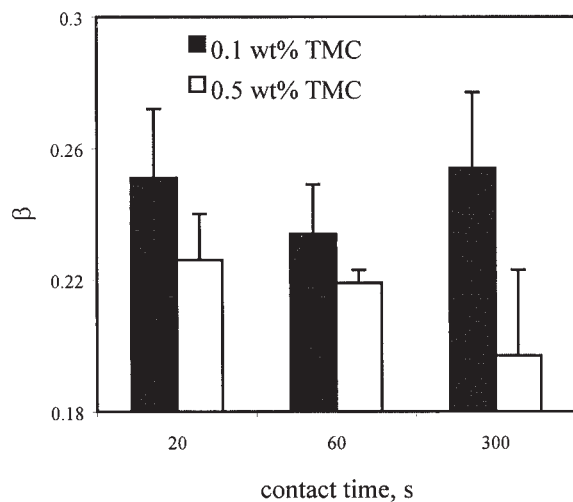

(a)
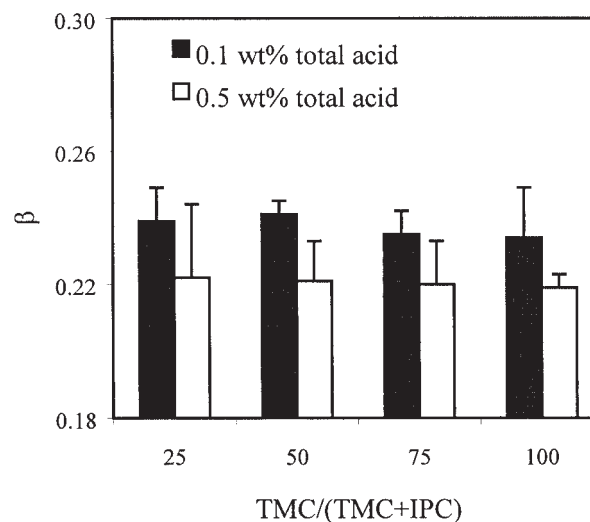
(b)

Figure 7 Effect of the organic-phase functionality on values of τ and β. The organic-phase functionality was varied systematically by using different fractions of TMC (by weight) in a TMC–IPC mixture. For these experiments, the MPD concentration and the contact time were held constant at 2 wt % and 1 min, respectively.

(a)

(b)

Figure 8 Effect of contact time on values of τ and β. For these experiments, the MPD concentration was held constant at 2 wt %. Results for two TMC concentrations, 0.1 and 0.5 wt %, respectively, are shown.

rates as a characteristic of IP film formation.[1,2] However, recent work by Freger[3,23] suggested that the time scale for IP reactions may be longer than previously reported. Although the results obtained here may provide support for Freger's assertion, they must be interpreted with caution given the unique polymerization conditions characteristic of the PDMA configuration.

Transport experiments

Although the PDMA methodology offers certain unique advantages for performing transport experi-

ments, there are significant differences between the PDMA transport (PDMA-T) and conventional permeation measurements. Whereas high *trans*-membrane pressure drops are used for conventional measurements, in PDMA-T water transport occurs because of a low osmotic pressure difference. In addition, water transport in PDMA-T occurs from the organic side of the IP film to the aqueous side, a direction that is opposite to that in conventional desalination by reverse osmosis (RO). Moreover, because the PDMA-T measurements are performed on the as-formed barrier layer, the hydration state of the barrier layer may be different from that for commercial IP films. A limitation of the PDMA-T measurements is that only the solvent (water) transport through the barrier layer can be measured and rejection values cannot be obtained. In spite of these differences, such transport measurements are valuable because they complement the results obtained from stress-relaxation experiments, and together provide a more complete understanding regarding the relationship between the network structure and the intrinsic transport behavior of the barrier layer.

Effect of TMC concentration

PDMA-T solvent (water) permeation measurements were performed on IP barrier layers formed from five different TMC concentrations, each in combination with a 2 wt % aqueous MPD solution. Statistical analysis of the results indicated that values of the membrane constant A were highest and essentially constant as the TMC concentration was increased from 0.01 through 0.1 wt % but decreased for TMC concentrations > 0.1 wt % (Fig. 9).
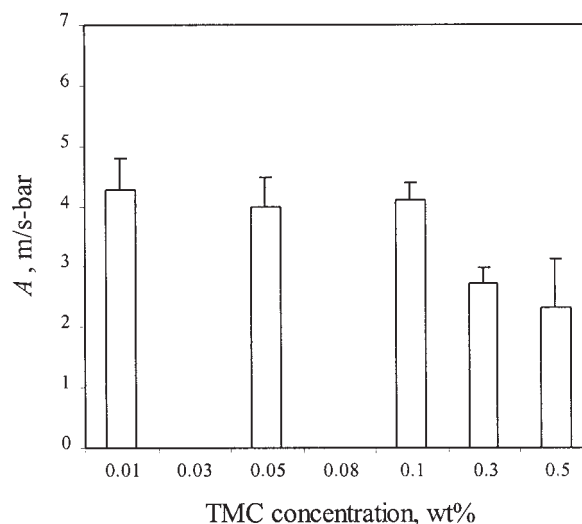
Figure 9 Effect of the TMC concentration on the membrane constant A. The MPD concentration was held constant at 2 wt %.

According to the solution–diffusion mechanism, solvent and solute transport through RO barrier layers will be governed by three factors: the solubility, the diffusivity, and the barrier-layer thickness.[24,25] If the as-formed barrier layers are in a swollen state, water solubility within the barrier layers should not be significantly affected by changes in the TMC concentration. In contrast, water diffusivity should be influenced by water–polymer interactions, and hence by the network structure.

The literature indicates that water permeation in the FT-30 polyamide TFC membrane is influenced by the free carboxyl groups that give the membrane a mildly acidic character.[2,23] Now, the degrees of crosslinking as well as branching should affect the concentration of the carboxyl groups; crosslinking would result in fewer free carboxyl groups because it involves the reaction of the pendant acid chloride group, which would otherwise be available for hydrolysis. In contrast, branching could result in more free carboxyl groups, given that a dangling branch would have two pendant unreacted acid chloride groups available for hydrolysis. The stress-relaxation experiments suggest that the degree of crosslinking is highest at an intermediate TMC concentration of 0.1 wt % and that the degree of branching monotonically increases with an increase in the TMC concentration. If the stress-relaxation experiments accurately reflect changes in the network structure, then water permeation should be adversely affected by greater TMC concentrations in the organic phase. Indeed, this effect was reported by Chai and Krantz,[22] who also observed that the water flux decreased for membranes made from TMC concentrations > 0.1 wt %.

Overall, the PDMA-T measurements support the insights obtained from the stress-relaxation experiments, and suggest the following relationship between polymer structure and water transport. At very low TMC concentrations (<0.1 wt %), a loose polyamide network is formed, whereby the water–polymer interactions would be relatively small. Hence, at low TMC concentrations, water permeation is relatively high and nearly constant. At a TMC concentration of 0.1 wt %, the degree of crosslinking is greatest and the extent of branching is relatively high, and thus the water permeation decreases.

Effect of organic-phase reactant functionality

As with the stress-relaxation experiments, a constant MPD concentration of 2 wt % and a constant contact time of 1 min were used in this set of experiments, and the organic-phase functionality was altered by using different IPC and TMC proportions in the organic phase. These results are shown in Figure 10, where the membrane constant A is plotted as a function of the TMC proportion in the organic phase. Trends in the
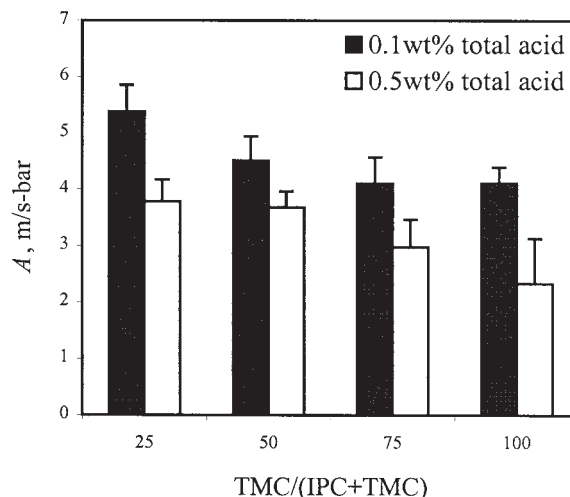
Figure 10 Effect of the organic-phase reactant functionality on A. The MPD concentration was maintained constant at 2 wt %.

data indicate that A decreases with increasing TMC proportion and that the A values were lower for 0.5 wt % total acid concentration compared to corresponding values for 0.1 wt % total acid concentration. Although statistical analysis confirmed the latter, only the 25% TMC proportion (0.1 wt % total acid concentration) results in a significantly higher A value than the higher proportions.

In general, the PDMA-T results are consistent with the observed stress-relaxation behavior. The stress-relaxation experiments suggested that increases in the TMC proportion beyond 25% do not produce significant increases in crosslinking. Thus, A is larger at a TMC proportion of 25% because this corresponds to the formation of a less-extensive network compared with the higher proportions of trifunctional monomer. In addition, because greater TMC concentrations lead to an increased degree of branching, A values are smaller at 0.5 wt % total acid concentration than corresponding values at 0.1 wt % total acid concentration.

CONCLUSION

The stress-relaxation and transport experiments conducted using PDMA on unsupported IP polyamide barrier layers yield important insights regarding the molecular structure and its relationship with water permeation behavior. Overall, the results of this study suggest the following:

- The degree of crosslinking is relatively insensitive to the concentration of difunctional amine (MPD) in the aqueous phase.
- Both crosslinking and branching depend on the trifunctional acid chloride (TMC) concentration in the organic phase. The degree of crosslinking

reaches a maximum for an intermediate TMC concentration (0.1 wt %), whereas the degree of branching increases monotonically with increasing TMC concentration.

- Beyond a certain minimum concentration of TMC in the organic solution (25 wt %), the network structure seems to be relatively insensitive to the proportion of TMC in a mixture incorporating a difunctional monomer (IPC) of similar structure.
- Very low MPD and TMC concentrations result in rather "loose" networks, in which the water flux is high and independent of the TMC concentration. However, in the barrier layers obtained from higher TMC concentrations, water permeation depends on the degree of branching within the network; higher degrees of branching result in lower water fluxes. This underscores the importance of the water–polymer interactions within the barrier layer.

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