

# Effect of Hydrophobic Hexafluoroisopropylidene Group on the Water Sorption Behaviors of Rigid Poly(*p*-phenylene pyromellitimide) Polyimide Thin Films

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**ABSTRACT:** We prepared poly(*p*-phenylene pyromellitimide) (PMDA–PDA), poly(*p*-phenylene 4,4'-hexafluoroisopropylidene diphthalimide), and their copolyimides with various compositions to explore the relationship between the water sorption and structure. The water sorption behaviors were gravimetrically investigated as a function of composition and temperature and interpreted with a Fickian diffusion model in films. Overall, the water sorption behaviors were strongly dependent on the changes in morphological structure, which originated from the variations in composition. When the content of the bulky hexafluoroisopropylidene group (6FDA) was increased, the water uptake

decreased from 5.80 to 3.18 wt %, whereas the diffusion coefficient increased from  $3.6 \times 10^{-10}$  to  $11.3 \times 10^{-10}$  cm<sup>2</sup>/s. The relatively high water uptake in the PMDA–PDA polyimide film was successfully healed by the incorporation of 6FDA, which may have resulted from the increases in the intermolecular packing order and hydrophobicity. The degree of orientation and crystallinity, which are in-plane characteristics, were directly correlated to the diffusion coefficient and activation energy in the polyimide film. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3442–3446, 2003

**Key words:** diffusion; activation energy; morphology

## INTRODUCTION

Since poly(4,4'-oxydiphenylene pyromellitimide) was introduced in the early 1960s, aromatic polyimides have been extensively used in the microelectronics industry as interdielectric layers, passivation layers, and alpha-particle barriers because of their excellent chemical and physical properties.<sup>1–4</sup> In particular, fully rod-like polyimides have gained great attention from both industry and academia because they can potentially provide a high modulus and high strength as well as a high dimensional stability. A representative fully rod-like polyimide is poly(*p*-phenylene pyromellitimide) (PMDA–PDA). PMDA–PDA polyimide exhibits a high chain rigidity and relatively low stress and is thermally stable up to about 600°C, both of which are required in the fabrication of microelectronic devices. Even though PMDA–PDA has a low chemical affinity to water, it exhibits a relatively high water sorption,<sup>5–7</sup> which causes potential reliability problems in microelectronic devices,<sup>8–10</sup> such as displacement, package crack, delamination, loss of adhesion, potential corrosion, and mechanical failures in thin films. Therefore, the phenomenon of water sorption is an interesting subject in the design and selec-

tion of advanced structural materials for the fabrication of microelectronic devices with better performance and reliability.

In this study, we attempted to improve its water sorption properties by incorporating a hydrophobic hexafluoroisopropylidene group into the PMDA–PDA polymer backbone, which could significantly change the chemical and morphological structures of the film. The water sorption behaviors were gravimetrically investigated with a thin film diffusion analyzer.<sup>7,11–15</sup> The water sorption results were analyzed with a Fickian diffusion model in thin films and were interpreted in terms of the chemical and morphological structures.

## EXPERIMENTAL

Poly(amic acid) solutions of pyromellitic dianhydride (PMDA)/4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA)-*p*-phenylene diamine (PDA) polyimides with various 6FDA compositions were prepared with an equimolar amount of a dianhydride or a combination of dianhydrides (PMDA/6FDA) with a PDA diamine. The synthetic routes and chemical structure are shown in Figure 1. The obtained poly(amic acid) solutions were spin-coated on silicon substrates and were then prebaked on a hot plate at 80°C for 30 min. The prebaked films were thermally imidized at 150°C for 30 min, 230°C for 30 min, 300°C for 30 min, and 400°C for 60 min. The film thickness (*L*), which was measured with a surface profiler (Tencor Instruments Co., model AS 500, San Jose, CA), was

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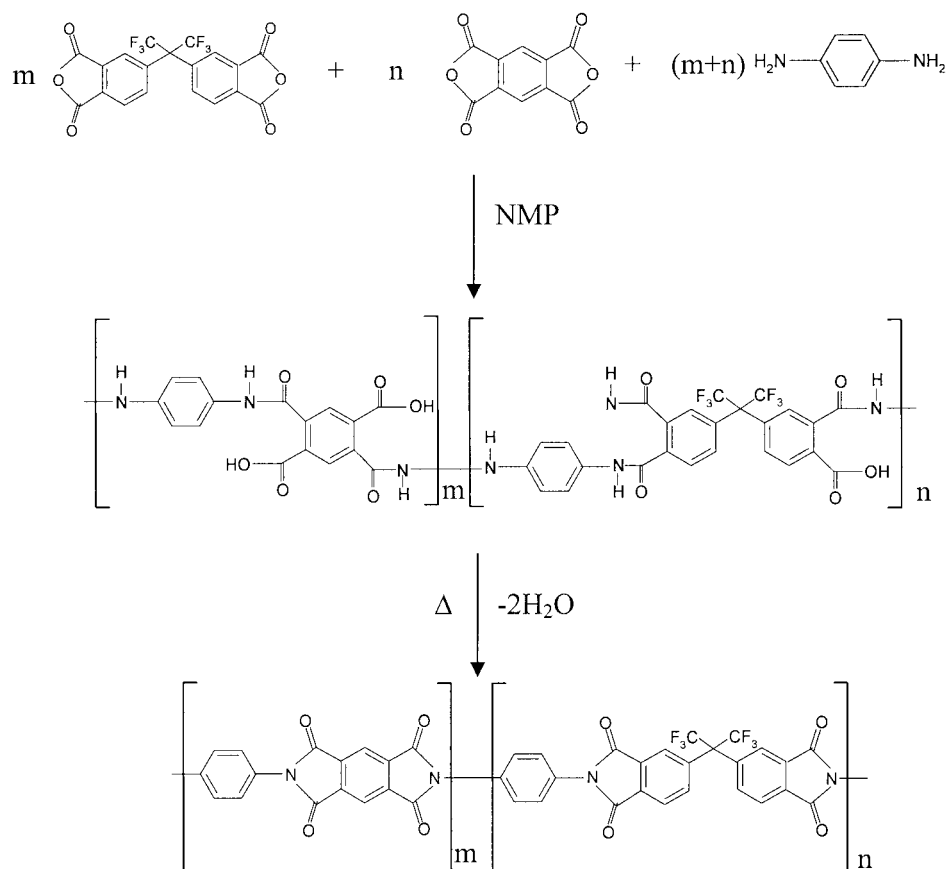


Figure 1 Synthetic routes and chemical structures of the PMDA-6FDA/PDA polyimides.

11–14  $\mu\text{m}$ . Then, the films were taken off of the substrates with the aid of deionized water and were then dried for 24 h at 80°C.

The water sorption behaviors of the fully cured polyimide thin films were gravimetrically measured with a home-made thin film diffusion analyzer, as described in our previous articles.<sup>6,7,11–15</sup> Measurements were carried out at various temperatures from 5 to 60°C. The morphological structure of the films was measured with a wide-angle X-ray diffractometer (Rigaku Co., model RINT 2500H, Tokyo, Japan) and a prism coupler (Metriton, Inc., model 2010, Pennington, NJ). More details are available in our previous articles.<sup>11–15</sup>

## RESULTS AND DISCUSSION

Figure 2 shows the water sorption isotherms for the PMDA/6FDA-PDA polyimide films, which were measured at 25°C and 100% relative humidity. The experimental data were apparently well-fitted to a theoretical Fick's law relation:<sup>16</sup>

$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left(\frac{-D(2m+1)^2\pi^2 t}{L^2}\right) \quad (1)$$

where  $M(t)$  and  $M(\infty)$  are the masses sorbed at time  $t$  and at infinite time, respectively,  $M$  is an integer, and  $D$  is the diffusion coefficient. Thus,  $D$  and water uptake were simulated with eq. (1) and are summarized in Table I and Figure 3.

The water uptake varied in the range 5.80 to 3.18 wt %, apparently decreasing as the 6FDA content increased. This indicates that the relatively high water uptake in the PMDA-PDA polyimide film was healed

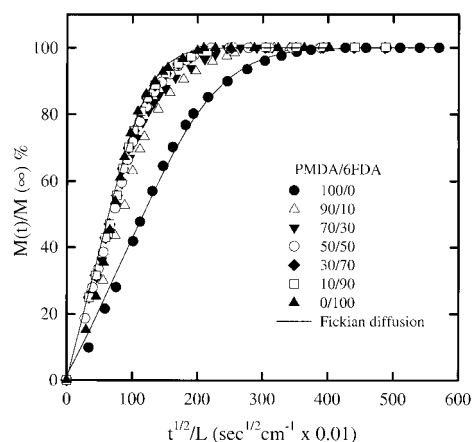


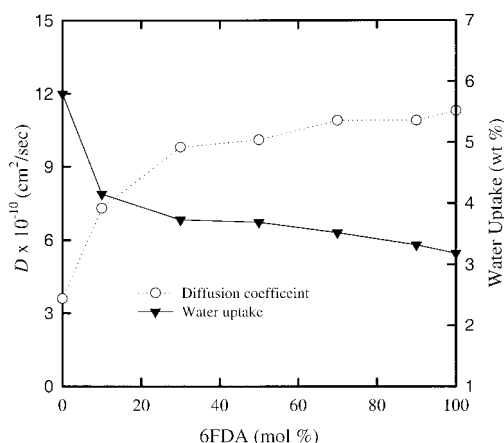
Figure 2 Water sorption isotherms of the PMDA/6FDA-PDA polyimide films measured at 25°C and 100% relative humidity.

**TABLE I**  
Water Uptake and  $D$  of the PMDA/6FDA-PDA Polyimide Films Measured at 25°C and 100% Relative Humidity

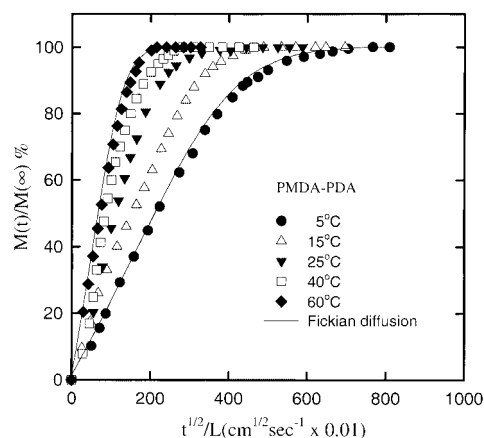
Molar ratio PMDA/6FDA	$L$ ( $\mu\text{m}$ )	$D \times 10^{-10}$ ( $\text{cm}^2/\text{s}$ )	Water uptake (wt %)	$E_a$ (kcal/mol)
100/0	12.2	3.6	5.80	7.63
90/10	13.0	7.3	4.15	6.79
70/30	12.0	9.8	3.73	—
50/50	13.0	10.1	3.69	6.07
30/70	13.5	10.9	3.52	—
10/90	12.8	10.9	3.32	5.89
0/100	11.7	11.3	3.18	5.82

by the incorporation of the hydrophobic hexafluoroisopropylidene 6FDA group. However,  $D$  showed different trends with the water uptake.  $D$  increased from  $3.6 \times 10^{-10}$  to  $11.3 \times 10^{-10} \text{ cm}^2/\text{s}$  with increasing content of 6FDA. This may have come from differences in the critical factors affecting  $D$  and water uptake. It is possible that  $D$  was closely related to the in-plane morphological structure (in-plane orientation), whereas the water uptake was affected by the out-of-plane morphological structure (packing order).<sup>14,15</sup>

The water sorption isotherms for different compositions of PMDA/6FDA-PDA polyimide films were further measured over a temperature ranges of 5–60°C. The results for the PMDA-PDA films are presented in Figure 4. With increasing temperature,  $D$  increased from  $1.5 \times 10^{-10}$  to  $12.6 \times 10^{-10} \text{ cm}^2/\text{s}$  and apparently increased with increasing temperature. Similar results with  $D$  in the PMDA-PDA polyimide film were observed for the PMDA/6FDA-PDA polyimide films with other compositions [see Fig. 5 (a)]. These increases indicate that the polymer chains at higher temperatures could have been more mobile or flexible and then could have made water molecules more penetrable, which may have led to the increase



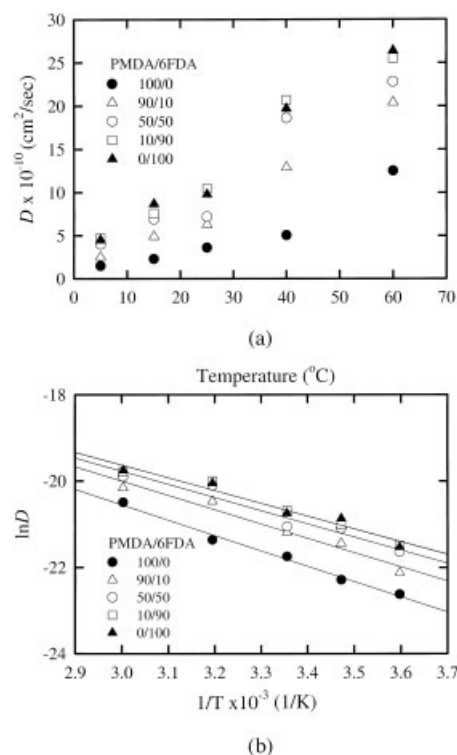
**Figure 3**  $D$  and water uptake of the PMDA/6FDA-PDA polyimide films measured at 25°C and 100% relative humidity.



**Figure 4** Water sorption isotherms of the PMDA-PDA polyimide films measured in various temperatures from 5 to 60°C.

in  $D$ .<sup>13,15,17</sup> However, the effect of temperature on  $D$  was strongly dependent on the composition of the PMDA/6FDA-PDA polyimide films.

We calculated the activation energy ( $E_a$ ) for the water diffusion from  $D$ s on the basis of the Arrhenius form by fitting the dependence of  $\log D$  on reciprocal temperature.<sup>14,16</sup>  $E_a$  was needed to enable water molecules to diffuse through polymer chains. As shown in Figure 5(b), the plots of  $\ln D$  versus  $1/T$  exhibited a fairly linear relationship, which implies that the diffusion mechanism of water did not change with temperature.<sup>18</sup>  $E_a$  was 7.63 kcal/mol for PMDA-PDA and 5.82



**Figure 5** (a)  $D$ s as a function of temperature and (b) Arrhenius plots of  $D$  in the polyimide films.

**TABLE II**  
Refractive Indices and  $\Delta$  of the PMDA/6FDA-PDA Polyimide Films

Molar ratio PMDA/ 6FDA	$L$ ( $\mu\text{m}$ )	Refractive indices at 632.8 nm			
		$n_{xy}$	$n_z$	$n_{av}$	$(\Delta)^b$
100/0	12.2	1.8244	1.5827	1.7438	0.2397
90/10	13.0	1.7256	1.5795	1.6769	0.1461
70/30	12.0	1.6976	1.5787	1.6580	0.1189
50/50	13.0	1.6458	1.5681	1.6199	0.0777
30/70	13.5	1.6083	1.5650	1.5939	0.0433
10/90	12.8	1.6002	1.5648	1.5913	0.0354
0/100	11.7	1.5844	1.5734	1.5807	0.0110

$$^a n_{av} = (2n_{xy} + n_z)/3;$$

$$^b \Delta = n_{xy} - n_z/t.$$

kcal/mol for 6FDA-PDA. The copolyimides showed intermediate values between those of homopolyimides. Apparently,  $E_a$  in the PMDA/6FDA-PDA polyimide films decreased with increasing content of 6FDA. This indicates the reduced ability of water molecules to diffuse through the copolyimide thin films with less 6FDA. Specifically, the PMDA-PDA polyimide films showed high  $E_a$ 's, which led to low  $D$ s.

These water sorption behaviors could be attributed to the difference in the chemical structure and/or morphology. By comparing the chemical structures of the PMDA-PDA and 6FDA-PDA, we attributed the low water uptake in the 6FDA-PDA polyimide film to the presence of the hexafluoroisopropylidene linkage [ $-\text{C}(\text{CF}_3)_2$ ], which could be treated as an unfavorable site to water molecules because it was hydrophobic.<sup>10</sup> However,  $D$  increased and  $E_a$  decreased with increasing content of the hydrophobic 6FDA. This suggests that the water sorption may have been significantly affected by the changes in morphological structure; crystallinity, in-plane orientation, and packing order.<sup>11-15,17</sup>

### Morphological structure

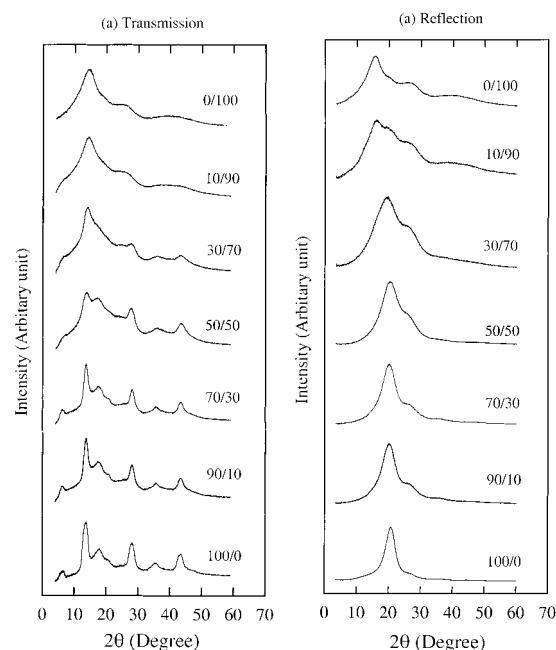
The water sorption behaviors may have resulted from the changes in morphological structure by the variation of composition in the PMDA/6FDA-PDA polyimide films. The refractive indices and film birefringence ( $\Delta$ )<sup>11-15</sup> were obtained with a prism coupler (see Table II). The in-plane refractive index ( $n_{xy}$ ) was always higher than the out-of-plane refractive index ( $n_z$ ), regardless of the composition of the copolymers. This indicates that polymer chains were preferentially aligned in the film plane. However, with increasing 6FDA content, the  $n_{xy}$  and  $n_z$  decreased, consequently leading to decreases in the average refractive index ( $n_{av}$ ) and  $\Delta$ . This indicates that the molecular in-plane orientation degraded as the content of 6FDA increased. In fact, the PMDA-PDA had only a rod-like conformation with a limited rotational freedom, resulting in an inherent high chain order along the chain axis and a high degree of in-plane orientation. The

decreases in the  $n_{av}$  and  $\Delta$  for the copolyimide films containing 6FDA may have resulted from the disturbance of the molecular in-plane orientation due to the bulky hexafluoroisopropylidene groups.

The morphological structure of the fully cured polyimide films was further analyzed by wide-angle X-ray diffraction (WAXD; transmission and reflection geometries). Here, the transmission pattern gave structural information for the film plane, whereas the reflection pattern gave structural information for the out-of-film plane.<sup>14,15,19</sup> The results are depicted in Figure 6.

As shown in Figure 6(a), the PMDA-PDA polyimide film showed multiple (001) diffraction peaks and one amorphous halo peak in the transmission pattern, indicating that the polymer chains of PMDA-PDA were mainly oriented in the film plane and that PMDA-PDA had a high degree of order and good in-plane orientation due to the rod-like chain nature. However, the transmission pattern in the PMDA-PDA was strongly affected by the incorporation of the bulky 6FDA. The (001) diffraction peaks in the transmission pattern became weak and broadened as the 6FDA content increased and almost disappeared for the copolyimide films incorporating over 50 mol % 6FDA. This indicates that the order in the film plane and molecular in-plane orientation degraded as the content of 6FDA increased, which may have been caused by the hindrance effect of the bulky  $-\text{C}(\text{CF}_3)_2$  group in the polymer chains.<sup>2,10</sup> These results show good agreement with the results of  $\Delta$  by prism coupling analysis.

The reflection patterns for the PMDA/6FDA-PDA polyimide films, however, were quite different from the transmission patterns, as shown in Figure 6(b). The



**Figure 6** WAXD patterns of the PMDA/6FDA-PDA polyimide films.



reflection pattern for the PMDA-PDA polyimide exhibited only one amorphous halo peak at  $21^\circ$  ( $2\theta$ ), indicating that the PMDA-PDA had a poor packing order. Despite a high in-plane orientation, the poor packing order of PMDA-PDA may have been caused by limited chain mobility or chain relaxation, which is closely related to the glass-transition temperature ( $>500^\circ\text{C}$ ). Because of the high glass-transition temperature over the final temperature of curing process, for the PMDA-PDA there was very limited mobility and a lower degree of chain relaxation to permit any chain organization, which may have resulted in poor packing and morphological defects for the water sorption.<sup>6,7</sup> Although similar reflection patterns were observed for the remaining copolyimide films containing 6FDA, additional shoulder diffraction peaks at  $20\text{--}30^\circ$ , which may have been related to the intermolecular packing order, were found as the content of 6FDA increased. From the peaks of this range in the reflection pattern, we speculated that the packing order increased with increasing 6FDA, and the morphological defects for the water sorption of the PMDA-PDA were more or less healed.

As shown by the WAXD and refractive indices results, the morphological structure of the PMDA/6FDA-PDA homopolyimide and copolyimide films was significantly changed by the variation of the composition. The intermolecular packing order in the films was enhanced by the increase in the content of 6FDA, whereas the molecular in-plane orientation was degraded. Thus, the lower water uptake in films with higher contents of 6FDA may have resulted mainly from the enhancements of intermolecular packing order. However,  $D$  and  $E_a$  showed opposite trends with water uptake. This may have come from the difference in critical factors affecting  $D$  and water uptake. The diffusion behaviors of water molecules into the film might have occurred predominantly in the direction perpendicular to the film plane and, thus, might have been affected by the in-plane morphological structure. The crystallinity and in-plane orientation of PMDA-PDA were degraded as the content of 6FDA increased, which means that the films with higher contents of 6FDA had fewer sites for water diffusion and reduced abilities of water molecules to squeeze between polymer chains. Thus, this may have led to a slow diffusion rate and a high  $E_a$  in the films with lower contents of 6FDA.

## CONCLUSIONS

In this study, we attempted to improve the water sorption properties of fully rod-like PMDA-PDA polyimide films by incorporating hydrophobic hexafluoroisopropylidene groups ( $-\text{C}(\text{CF}_3)_2$ ) into the polymer backbone. For this, different compositions of

PMDA/6FDA-PDA homopolyimides and copolyimides were synthesized in thin films. Their water sorption properties were correlated with their structures, which were characterized by X-ray diffraction and refractive index/ $\Delta$  measurements. With increasing bulky 6FDA, the water uptake decreased from 5.80 to 3.18 wt %, whereas  $D$  increased from  $3.6 \times 10^{-10}$  to  $11.3 \times 10^{-10}$   $\text{cm}^2/\text{s}$ . The water sorption behaviors may have resulted from the morphological variations in the films, such as polymer chain order, in-plane orientation, and intermolecular packing order, depending on the polymer compositions. Higher contents of 6FDA in PMDA/6FDA-PDA copolyimide films gave lower molecular in-plane orientation and crystallinity, resulting in an increase in  $D$  and a decrease in  $E_a$ . In contrast, the polyimide films with higher contents of 6FDA, which had a higher intermolecular packing order and an increased hydrophobicity, absorbed water less. We conclude that the molecular packing order and the chemical affinity to water molecules were the predominant factors that controlled the water uptake in the PMDA/6FDA-PDA copolyimides.

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