

Water-Sorption Behavior of *p*-Phenylene Diamine-Based Polyimide Thin Films

JONGCHUL SEO, ANNA LEE, CHOONKEUN LEE, HAKSOO HAN

Department of Chemical Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-Gu, Seoul 120-749, Korea

Received 5 April 1999; accepted 15 October 1999

ABSTRACT: Four different *p*-PDA-based polyimide thin films were prepared from their respective poly(amic acid)s through thermal imidization at 400°C: poly(*p*-phenylene pyromellitimide) (PMDA-PDA); poly(*p*-phenylene biphenyltetra carboximide) (BPDA-PDA); poly(*p*-phenylene 3,3',4,4'-oxydiphthalimide) (ODPA-PDA); and poly(*p*-phenylene 4,4'-hexafluoroisopropylidene diphthalimide) (6FDA-PDA). Water-sorption behaviors of polyimide films were gravimetrically investigated at 25°C and 22–100% relative humidity by using the modified electromicrobalance (Thin Film Diffusion Analyzer). The diffusion coefficients of water for the polyimides varies in the range of 1.6 to 10.5×10^{-10} cm²/s, and are in the increasing order: BPDA-PDA < PMDA-PDA ~ ODPA-PDA < 6FDA-PDA. The water uptakes of polyimides vary from 1.46 to 5.80 wt %, and are in the increasing order: BPDA-PDA < ODPA-PDA < 6FDA-PDA < PMDA-PDA. The water-sorption behaviors for the *p*-PDA-based polyimides are closely related to the morphological structure; specifically, the diffusion coefficients in *p*-PDA-based polyimide thin films are closely related to the in-plane orientation and mean intermolecular distance, whereas the water uptakes are affected by the packing order. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1315–1323, 2000

Key words: water sorption; morphological structure; chemical structure; diffusion coefficient; *p*-phenylene diamine

INTRODUCTION

High-temperature aromatic polyimides are used in the fabrication of microelectronic devices, such as interdielectric, α -particle-protecting, and passivation layers, because of their characteristic relatively high thermal stability, high chemical resistance, and excellent mechanical toughness that result from the aromatic ring and imide ring units on the chain backbone.^{1–4} In the development of advanced materials, knowledge of environmental effects on the behavior of high-performance polyimide is essential for the design and selection of structural materials. However, de-

spite their relatively high chemical resistance characteristics, polyimides still absorb water in some amounts.^{5–12} Specifically, water absorbed in polyimide films not only causes problems in reliability,^{2–5} such as displacement, package cracking, delamination, loss of adhesion, potential corrosion, and mechanical failures in thin films, but may also place processing constraints on device fabrication. On uptake of water in polyimide films, the dielectric constants and conductivities, as well as the level of dielectric loss, will increase.^{5,6} As to retaining or improving the dielectric property, water uptake in films should be minimized. Water-sorption behaviors are also closely related to the stress relaxation in polyimide thin films.^{8,11} Therefore, the phenomenon of water sorption is an interesting subject in the design and selection of advanced structural ma-

Correspondence to: H. Han (hshan@bubble.yonsei.ac.kr).

Journal of Applied Polymer Science, Vol. 76, 1315–1323 (2000)
© 2000 John Wiley & Sons, Inc.

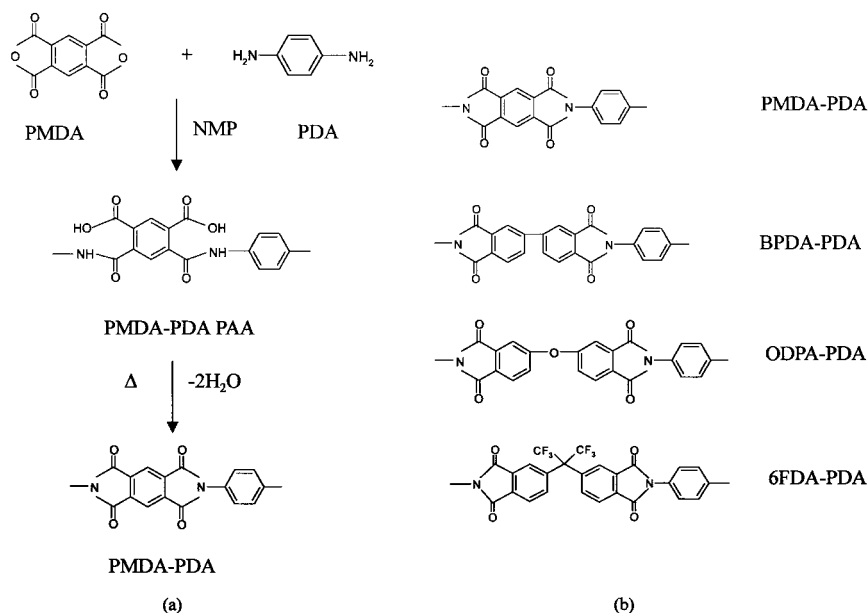


Figure 1 Schematic of polyimides prepared from their respective poly(amic acid) precursors: (a) synthesis, (b) chemical structures.

materials for the fabrication of advanced microelectronic devices with higher performance and better reliability. One possible criterion concerning choice of material for electronics applications might be based on how quickly and to what extent water permeates into it.

The water-sorption behaviors of polyimide thin films have been widely studied by several research groups using various methods.^{5–14} Generally, water sorption into polyimide films is probably dependent on the chemical and morphological structures, which originate in the processing history. The goal of this work is to characterize the water-sorption behavior in the *p*-PDA-based polyimide thin films. The water-sorption characteristics in thin films were investigated together with the chemical backbone structure and the morphological structure.

EXPERIMENTAL

Materials and Sample Preparation

p-Phenylenediamine (PDA), pyromellitic dianhydride (PMDA), biphenyltetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA), and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aldrich Chemical Co. and Chriskev Chemical Co. All the monomers were purified by

sublimation under reduced pressure or recrystallization. Poly(*p*-phenylene pyromellitic acid) (PMDA-PDA PAA) was prepared under nitrogen atmosphere by adding PMDA to PDA in anhydrous NMP as in previous studies^{1–3,11} [see Fig. 1(a)]. These solutions had a solids content of 15 wt %. Other poly(amic acid)s were prepared in the same manner as PMDA-PDA PAA was synthesized: poly(*p*-phenylene biphenyltetracarboxamic acid) (BPDA-PDA PAA), poly(*p*-phenylene 3,3',4,4'-oxydiphthalamic acid) (ODPA-PDA PAA), poly(*p*-phenylene 4,4'-hexafluoroisopropylidene diphthalamic acid) (6FDA-PDA PAA) [see Fig. 1(b)].

All the polyimide precursors were spin-coated on a silicon (100) substrate. Coated wafers were prebaked at 80°C for 30 min on a hot plate. The prebaked samples were then placed in the curing oven and cured by the following schedule^{8–11}: 150°C/30 min, 230°C/30 min, 300°C/30 min, and 400°C/60 min. The ramping rate was 2.5°C/min and cooling rate was 2.0°C/min for the curing process. The thickness was controlled in the range of 10–15 microns by a spin coater.^{13,15} The thickness of polyimide thin films was measured by using a surface profiler (Tencor Instruments Co., Model P-10). Then, the polyimide films were taken off from the substrates with the aid of deionized water and washed with distilled water several times and dried. The fully cured films were cut into rectangular pieces approximately 10

Table I Vapor Pressure and Relative Humidity of Aqueous Salt Solutions at 25°C

Aqueous Salt Solution	Equilibrium Vapor Pressure (mmHg)	Relative Humidity (%)
H ₂ O	23.76	100
Na ₂ CO ₃ · 6H ₂ O	20.90	87
KNO ₃	16.70	71
Mg(NO ₃) ₂ · 6H ₂ O	11.90	52
CaCl ₂ · 6H ₂ O	7.08	31
KC ₂ H ₃ O ₂ · (1.5)H ₂ O	5.35	22

× 15 mm and fully dried in vacuum to use for the water-sorption measurement.

Measurements

For the polyimide films, water-sorption behaviors were measured over 22–100% relative humidity (RH) at 25°C as a function of time, by using a Thin Film Diffusion Analyzer^{8–11} (Cahn Instruments Co., Model D-200) with a resolution of 0.1 μg. More detailed procedures are described in previous studies.^{8–11} Measurements were carried out in various humidities of 22–100% RH. Then, in various humidities of 22–100% RH, five different types of aqueous salt solutions were prepared in distilled water, as shown in Table I.

All the sorption isotherms were simulated with Fick's second law, which has been driven for an infinite slab with a constant surface concentration by Crank and associates^{16,17}:

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

where $M(t)$ is the water sorption at a time t , $M(\infty)$ is the water sorption at $t = \infty$, D is the mutual diffusion coefficient of water and polymer systems, and L is the film thickness. The diffusion coefficient is then consequently simulated by fitting eq. (1) to normalized experimental data. Water uptake means the amount of sorbed water per unit mass of dried film in equilibrium state.

For the morphological structure of polyimide thin films, wide-angle X-ray diffraction (WAXD) patterns were obtained by a horizontal X-ray dif-

fractometer (Rigaku Co., Model D/Max-200B) with nickel-filtered radiation. One diffractometer was set up for the transmission mode (i.e., reflections from lattice planes normal to the film surface) with a thin asymmetric cut (101) quartz-plate monochromator, bent to a section of a logarithmic spiral and located in the diffracted beam. The other was used for the reflection mode (i.e., reflections from lattice planes parallel to the film surface) with a curved graphite monochromator in the diffracted beam. The CuK_α radiation source ($\lambda = 1.54 \text{ \AA}$) was operated at 35 kV and 40 mA. All the WAXD measurements were carried out in $\theta/2\theta$ mode. The 2θ scan data were collected in the range of 5–60° at 0.02° intervals with a scan speed of 0.3–0.5° min⁻¹, depending on whether a reflection or transmission scan was being made. The measured X-ray diffraction intensities were corrected for the background run and then normalized for the film samples by matching the integrated intensity over the range of 58–60° (2θ).

RESULTS AND DISCUSSION

The water sorption for the *p*-PDA-based polyimide thin films, PMDA-PDA, BPDA-PDA, OPA-PDA, and 6FDA-PDA, were gravimetrically measured over 22–100% RH at 25°C. These results are given in Table II.

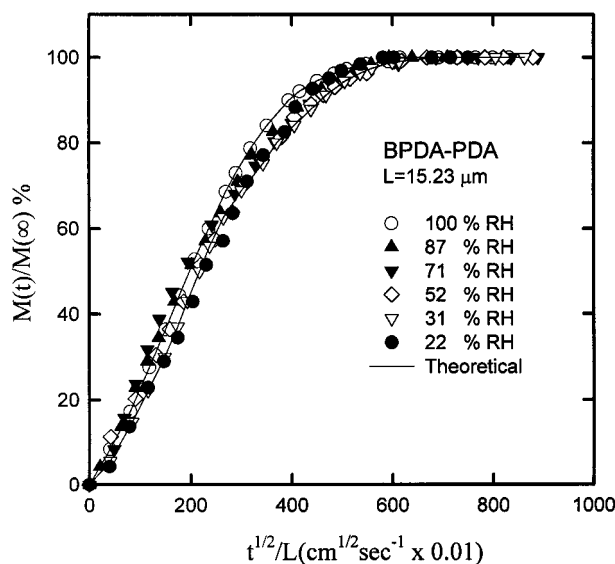
The isotherms of water sorption for BPDA-PDA were investigated with various relative humidities and plotted as a function of time, as shown in Figure 2. The sorption isotherms were reasonably well fitted to a Fickian diffusion model, irrespective of relative humidity and morphological heterogeneities.^{8–11,18–20} It shows that the sorption behavior of small molecules in polymers should be patterned after a Fickian diffusion model, well below the glass transition temperature of the host.^{16,17,21,22}

The diffusion coefficient for BPDA-PDA varied slightly in the range of 1.1 to 1.7 × 10⁻¹⁰ cm²/s over 22–100% RH. Apparently, the diffusion coefficients of water in BPDA-PDA polyimide thin film were nearly invariant with various humidities within experimental error, as shown in Figure 3. It indicates that the water diffusion in BPDA-PDA film apparently obeys Fick's second law, which assumes that the diffusion coefficient is constant and not a function of concentration in films. These are consistent with our previous results^{9,10} and several researchers' results.^{14,23}

Table II Diffusion Coefficients and Water Uptakes in Polyimide Thin Films Prepared from Poly(amic acid)s Based on *p*-PDA Diamine

Polyimide Structure	Thickness (μm)	Relative Humidity (%)	Diffusion Coefficient $D \times 10^{-10}$ (cm^2/s)	Water Uptake (wt %)
PMDA-PDA	12.20	22	3.6	1.09
		31	3.8	1.46
		52	3.6	2.65
		71	3.7	3.62
		87	4.1	4.51
		100	3.6	5.80
BPDA-PDA	15.23	22	1.4	0.28
		31	1.1	0.47
		52	1.1	0.84
		71	1.6	1.02
		87	1.3	1.37
		100	1.7	1.46
ODPA-PDA	13.02	22	4.1	0.35
		31	3.9	0.52
		52	3.8	0.92
		71	3.8	1.12
		87	4.2	1.42
		100	4.1	1.72
6FDA-PDA	11.72	22	11.0	0.60
		31	10.6	0.85
		52	11.4	1.35
		71	10.2	2.09
		87	11.1	2.50
		100	10.5	3.29

For the other polyimide thin films, PMDA-PDA, ODAPA-PA, and 6FDA-PDA, the water-sorption behaviors were investigated with the

**Figure 2** Isotherms of water sorption of 15.23- μm thick BPDA-PDA films measured over 22–100% RH at 25°C.

same technique; similar results with BPDA-PDA were observed, which were also independent of relative humidity and nearly invariant with humidity within experimental error, as shown in Figure 3. The diffusion coefficient varied slightly with humidity in the range of 3.6 to 4.1×10^{-10} cm^2/s for PMDA-PDA, 3.8 to 4.2×10^{-10} cm^2/s for ODPA-PDA, and 10.2 to 11.4×10^{-10} cm^2/s for 6FDA-PDA, respectively. The apparent diffusion coefficient of water in the polyimides as a function of relative humidity is approximately constant, which indicates that the water seems to be in a relatively constant environment regardless of the degree of water vapor concentration. It suggests that the polyimides are relatively homogeneous and the water is uniformly distributed in a more or less uniform manner. However, the diffusion coefficients of the *p*-PDA-based polyimide thin films with different dianhydrides are quite different from each other, strongly depending on the chemical structure of the polyimide.

The water uptake was measured for these polyimide thin films as a function of relative humidity. Surprisingly, the effects of relative humidity

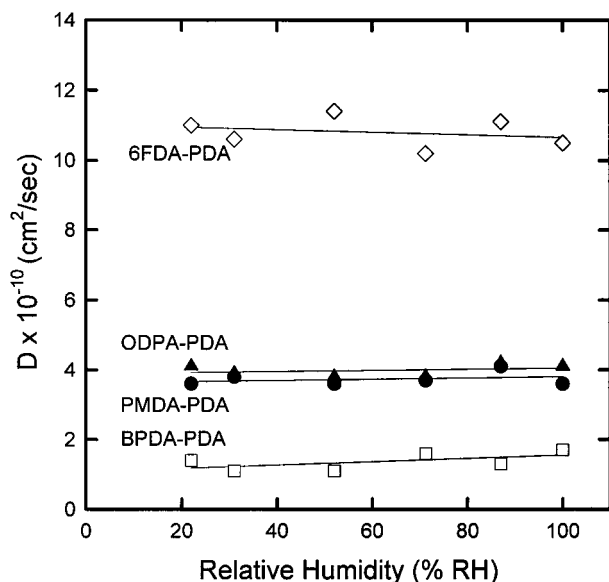


Figure 3 The effect of humidity on the diffusion coefficient of the *p*-PDA-based polyimide thin films measured at 25°C.

on the water uptake were significant, as shown in Figure 4. Water uptake is clearly a function of humidity for all the *p*-PDA-based polyimide thin films. For BPDA-PDA film, the water uptake increased with increasing relative humidity from 0.28 to 1.46 wt % in 22% and 100% RH, respec-

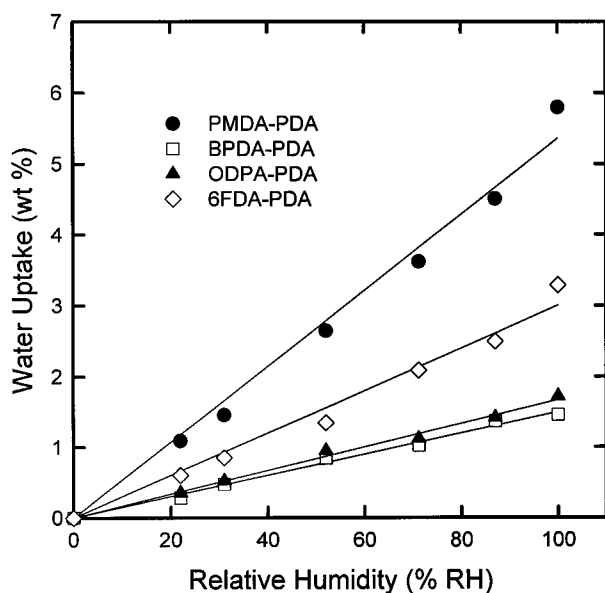


Figure 4 The effect of humidity on water uptakes of the *p*-PDA-based polyimide thin films measured at 25°C.

tively. For the other polyimide thin films, water uptake is nearly a linear function of relative humidity as with BPDA-PDA. It means that water-sorption mechanisms of the *p*-PDA-based polyimide thin films obey Henry's law.^{10,16,17} However, the water uptakes of polyimide thin films with different dianhydrides are quite different from each other, strongly depending on the chemical structure of the polyimide. Specifically, the value of water uptake for PMDA-PDA is always higher than that of the other polyimide thin films. It suggests that PMDA-PDA has chemical or morphological defects for the water sorption.^{8,11}

The effect of dianhydride chemical structure on the water sorption and the isotherms of the *p*-PDA-based polyimide thin films was measured at 100% RH and 25°C (depicted in Fig. 5). The diffusion coefficient of water in films varies in the range of 1.7 to 10.5 $\times 10^{-10}$ cm²/s, and is in the increasing order: BPDA-PDA < PMDA-PDA < ODPA-PDA < 6FDA-PDA. The water uptake varies from 1.46 to 5.80 wt %, and is in the increasing order: BPDA-PDA < ODPA-PDA < 6FDA-PDA < PMDA-PDA. The water-sorption isotherms of polyimide thin films with the same *p*-PDA diamine are quite different from each other, strongly depending on the chemical structure of the dianhydride. It may suggest that these sorption behaviors of water in the *p*-PDA-based polyimide thin films might be attributed to chemical affinity and morphological structure.⁸⁻¹⁵

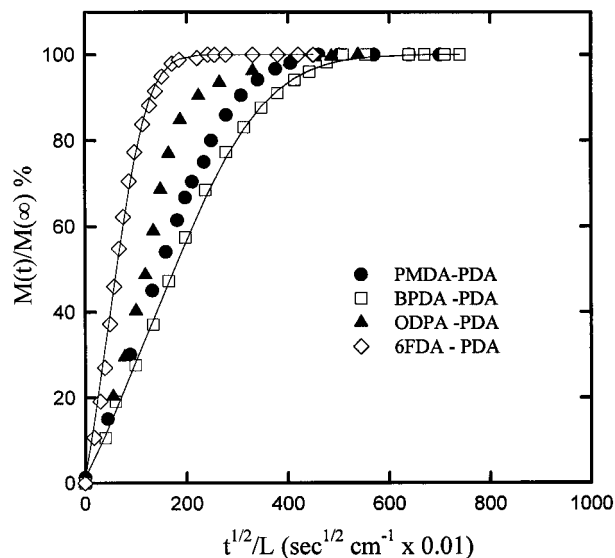


Figure 5 Isotherms of water sorption for the *p*-PDA-based polyimide thin films measured at 100% RH and 25°C.

Several researchers^{24–26} calculated the empirical solubility parameter δ of polyimides to water molecules by the group-contribution method of van Krevelen.¹⁶ Also, Han and associates^{8,27} experimentally introduced the chemical affinity to water molecules by measuring the surface energy. For the *p*-PDA-based polyimides, there are a great variety of sites and bonds for the polyimide chain at which water molecules can be bound, which make a big difference in the chemical affinity to water. Generally, molecules with similar values of the solubility parameter δ are more mutually soluble than molecules with disparate δ values.^{26,27} Hydrogen bonding and polar group may affect the solubility as well, because molecules dissolve more preferentially in hosts with similar degrees of hydrogen bonding.^{26,27} In this study, ODPA-PDA has a favorably hydrophilic group to which the water molecule is linked in the main chain, e.g., the ether group (—O—). However, the 6FDA-PDA polyimide has an unfavorably hydrophobic hexafluoroisopropylidene group [$-\text{C}(\text{CF}_3)_2$] linked to the water molecule in 6FDA dianhydride. In the units of $(\text{cal}/\text{cm}^3)^{1/2}$, the solubility parameter of water is 23.4. The values²⁶ of ether linkage and hexafluoroisopropylidene group are 14.51 and 4.15, respectively. From the chemical affinities and previous studies,^{8,25–27} one can simply expect that the water sorption in the *p*-PDA-based polyimide thin film is in the decreasing order: ODPA-PDA > PMDA-PDA > BPDA-PDA > 6FDA-PDA. Surprisingly, it shows that 6FDA-PDA, which has hydrophobic groups in the polymer chain, not only has a relatively higher water uptake than BPDA-PDA and ODPA-PDA, which have more hydrophilic groups, but also exhibits the highest diffusion coefficient of water, as shown in Figure 5. In addition, PMDA-PDA film shows relatively lower diffusion coefficients of water than does 6FDA-PDA film, which has the highest hydrophobicity. It is surprising that PMDA-PDA film exhibited high water uptake, which may suggest that water sorption of polyimide thin films may be significantly affected by morphological structure,^{8–11} including molecular order, chain orientation, and packing.

For the morphological structure of polyimide thin films, WAXD measurement (transmission and reflection patterns) was performed for the fully imidized polyimide films. The transmission patterns give structural information about the in-plane orientation of polyimide thin film, whereas the reflection patterns give structural information about the out-of-plane orientation of

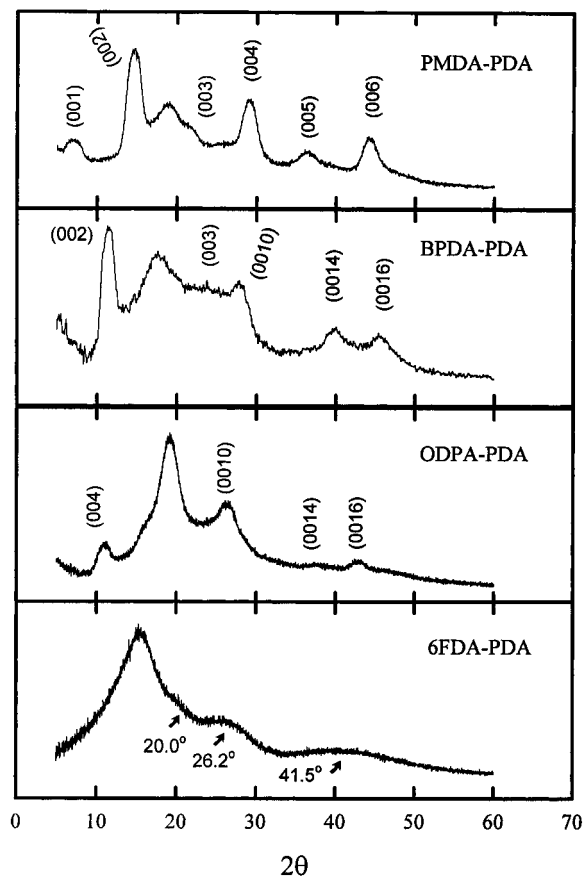


Figure 6 WAXD transmission patterns of the *p*-PDA-based polyimide films prepared from poly(amic acid) by thermal imidization at 400°C.

polyimide film.^{8–11,28} The results of WAXD measurement for the *p*-PDA-based polyimide thin films are depicted in Figures 6 and 7.

For the fully cured polyimide thin films, PMDA-PDA, BPDA-PDA, and ODPA-PDA, the transmission WAXD pattern shows multiple $(00l)$ diffraction peaks and one amorphous halo peak in the *c*-direction of the unit cell. It indicates that these polyimide films have a high degree of order and orientation of the chain axis direction parallel to the surface of the film.^{8–11} Specifically, the 6FDA-PDA transmission pattern exhibited no characteristic peaks, which indicates that 6FDA-PDA has an amorphous structure. In addition to the characteristic diffraction peaks, the mean intermolecular distances in the polyimide films^{28,29} were calculated from the characteristic transmission peaks, as shown in Table III. The mean intermolecular distance varies in the range of 4.72 to 5.68 Å, and is in the increasing order: PMDA-PDA ~ ODPA-PDA ~ BPDA-PDA < 6FDA-PDA.

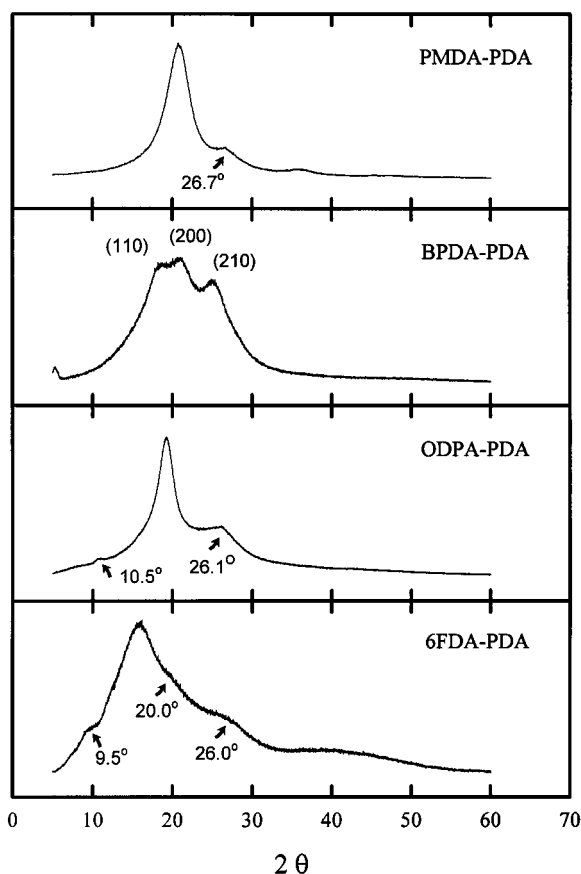


Figure 7 WAXD reflection patterns of the *p*-PDA-based polyimide films prepared from poly(amic acid) by thermal imidization at 400°C.

However, there exists no great difference in the mean intermolecular distance, except for 6FDA-PDA. From the transmission patterns and the mean intermolecular distances, it can be deduced not only that all the *p*-PDA-based polyimide films are anisotropic, but also that the imide chains are mostly aligned in the film plane and

highly ordered because of the high chain rigidity of the *p*-PDA diamine.²⁹ Specifically, 6FDA-PDA shows the greatest mean intermolecular distance in polymer chain. It may also show that the bulky $-\text{C}(\text{CF}_3)_2$ chain group hinders the order of interaction in the polymer and leads to an amorphous structure.

The reflection patterns for the *p*-PDA-based polyimide thin films, however, are quite different from the transmission patterns, as shown in Figure 7. The reflection WAXD pattern for the PMDA-PDA polyimide exhibited only one amorphous halo peak and a slight indication in an angle of 26.7°, which indicates that PMDA-PDA has poor packing order. In spite of high in-plane orientation and small mean intermolecular distance, the poor packing ordering of PMDA-PDA may be the result of the limited chain mobility or chain relaxation, which is closely related to the glass transition temperature (T_g). PMDA-PDA has a relatively high T_g ($>500^\circ\text{C}$) (Table III). As a result of the high T_g over the final temperature of curing process, for PMDA-DA, there will be very limited mobility and less degree of chain relaxation to permit any chain organization, which may result in poor packing and the morphological defects for water sorption.^{1,8,11,30–32} Although similar reflection patterns were observed for the ODPA-PDA and 6FDA-PDA polyimides, however, the additional shoulder diffraction peaks at ~ 9.5 – 10.5 and ~ 25.5 – 26.5° were found for the ODPA-PDA and 6FDA-PDA polyimides. Specifically, BPDA-PDA showed three (*hkl*) peaks in the reflection pattern, such as (110), (200), and (210). Of the diffraction peaks described earlier, the shoulder diffraction peak around 20– 30° in the reflection pattern may be related to the intermolecular packing order.¹¹ From the peaks of this range and characteristic

Table III Characteristics of Polyimide Films Prepared from Poly(amic acids) Based on *p*-PDA Diamine

Polymer Structure	Film Thickness (μm)	Glass Transition Temperature T_g^a ($^\circ\text{C}$)	Mean Intermolecular Distance ^b
PMDA-PDA	12.20	>500	4.72 Å (18.80°)
BPDA-PDA	15.23	360	4.81 Å (18.46°)
ODPA-PDA	13.02	380	4.72 Å (18.80°)
6FDA-PDA	11.72	350	5.68 Å (15.59°)

^a Obtained from References 2, 8, and 29.

^b Calculated from the peak maximum of amorphous halo in the transmission WAXD pattern.

diffraction peaks, it is speculated that the packing order in the *p*-PDA-based polyimides is in the increasing order: PMDA-PDA < 6FDA-PDA < ODPA-PDA < BPDA-PDA. This order is fairly consistent with that of water uptake in the *p*-PDA-based polyimides.

Therefore, it was found that the water-sorption behaviors for the *p*-PDA-based polyimides are closely related to the morphological structure. In particular, BPDA-PDA showed low diffusion coefficient and water uptake because of the high orientation and excellent interchain ordering. Whereas PMDA-PDA showed a relatively high water uptake resulting from the lesser degree of packing order, which may come from a high glass transition temperature, 6FDA-PDA showed a relatively higher diffusion coefficient resulting from the amorphous structure, although it has hydrophobic groups in the polymer chain.

CONCLUSIONS

For the fully cured *p*-PDA-based polyimide films, water-sorption behaviors were gravimetrically investigated. The diffusion coefficient, over the conditions investigated, is nearly invariant with humidity within experimental error, which indicates that a Fickian diffusion model with constant diffusion coefficient is valid for this work. For the *p*-PDA-based polyimide thin films, water uptake is nearly a linear function of relative humidity, which means that these polymers obey Henry's law. Water-sorption behaviors are quite different from each other, strongly depending on the chemical and the morphological structures. The water uptake varies from 1.46 to 5.80 wt %, and is in the increasing order: BPDA-PDA ~ ODPA-PDA < 6FDA-PDA < PMDA-PDA. In particular, the morphology of PMDA-PDA polyimide thin film shows a relatively lesser degree of packing by the restricted chain mobilities and low degree of chain relaxation resulting from high glass transition temperature. PMDA-PDA revealed a relatively higher water uptake. Conclusively, both the chemical and morphological structures are important parameters to control both water uptake and diffusion coefficient, which significantly affect the dielectric properties of polyimide films. However, the morphological structure is a more critical parameter than the chemical structure in controlling it. Of the morphological structure, the diffusion rates in films are closely related to the in-plane orientation and mean intermolecular

distance, whereas the water uptakes are affected by the packing order.

The authors would like to gratefully acknowledge the Korea Research Foundation (KRF) (Contract No. 1998-001-E01258) for the financial support of this work.

REFERENCES

- Bessonov, M. I.; Zubkov, V. A. *Polyamic Acids and Polyimides: Synthesis, Transformations, and Structure*; CRC Press: Boca Raton, FL, 1993.
- Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
- Feger, C.; Khojasteh, M. M.; Htoo, M. S. *Advances in Polyimide Science and Technology*; Technomic Publications: Lancaster, PA, 1993.
- Thompson, L. F.; Wilson, C. G.; Tagawa, S. in *Polymers for Microelectronics: Resist and Dielectrics*; ACS Symposium Series 537; American Chemical Society: Washington, DC, 1992.
- Melcher, J.; Daben, Y.; Arlt, G. *IEEE Trans Elect Insul* 1989, 24, 31.
- Bellucci, F.; Khamis, I.; Senturia, S. D.; Latanision, R. M. *J Electrochem Soc* 1990, 137, 1778.
- Yang, D. K.; Koros, W. J.; Hopfenberg, H. B.; Stannett, V. T. *J Appl Polym Sci* 1986, 31, 1619.
- Han, H.; Seo, J.; Ree, M.; Pyo, S. M.; Gryte, C. C. *Polymer* 1998, 39, 2963.
- Ree, M.; Han, H.; Gryte, C. C. *J Polym Sci Polym Phys* 1995, 33, 505.
- Han, H.; Gryte, C. C.; Ree, M. *Polymer* 1995, 36, 1663.
- Seo, J.; Han, H.; Kim, S.; Chung, H.; Joe, Y. I. *Polym J* 1999, 31, 127.
- Sacher, E.; Susko, J. R. *J Appl Polym Sci* 1979, 23, 2355.
- Jou, J. H.; Chang, Y. L.; Liu, C. H. *Macromolecules* 1992, 25, 5186.
- Denton, D. D.; Day, D. R.; Priore, D. F.; Senturia, S. D.; Anolick, E. S.; Scheider, D. *J Electron Mater* 1985, 14, 119.
- Jou, J. H.; Huang, P. T.; Chen, H. C.; Liao, C. N. *Polymer* 1992, 33, 967.
- Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford University Press, London, 1976.
- Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic Press: London, 1968.
- Isoda, I.; Shimada, H.; Kochi, M.; Kambe, H. *J Polym Sci Polym Phys* 1981, 19, 1293.
- Russell, T. P. *Polym Eng Sci* 1984, 24, 345.
- Russell, T. P. *J Polym Sci Polym Phys* 1984, 22, 1105.
- Frisch, H. L. *Polym Eng Sci* 1980, 20, 2.
- Hansen, C. M. *Polym Eng Sci* 1980, 20, 252.

23. Hubbell, W. H., Jr.; Brandt, H.; Munir, Z. A. *J Polym Sci Polym Phys* 1975, 13, 493.
24. Okamoto, K. I.; Tanihara, N.; Watanabe, H.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y.; Nakagawa, K. *J Polym Sci Polym Phys* 1992, 30, 1223.
25. van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier Science: Amsterdam, 1990.
26. Okamoto, K. I.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y. *J Polym Sci Polym Phys* 1989, 27, 1221.
27. Ree, M.; Han, H.; Gryte, C. C. *High Perform Polym* 1994, 6, 321.
28. Cullity, B. D. *Elements of X-ray Diffraction*, 2nd ed.; Addison-Wesley: London, 1977.
29. Ree, M.; Kim, K.; Woo, S. H.; Chang, H. *J Appl Phys* 1997, 82, 698.
30. Numata, S.; Fujisaki, K.; Kinjo, N. *Polymer* 1987, 28, 2282.
31. Numata, S.; Kinjo, N. *Polym Eng Sci* 1988, 28, 906.
32. Han, H. Ph.D. Dissertation, Columbia University, 1993.