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Water diffusion and sorption in films of high-performance poly(4,4′-oxydiphenylene pyromellitimide): effects of humidity, imidization history and film thickness

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Poly(4,4′-oxydiphenylene pyromellitimide) (PMDA–ODA) films of 10–109 μm thickness were prepared from its poly(amic acid) precursor by thermal imide-ring-closure formation at various temperatures. Water sorption in the films was measured at 25°C over 22–100% relative humidity using an electromicrobalance. Water diffusion in all the films was a nearly Fickian process despite the morphological heterogeneity due to the ordered and less ordered phases. Depending upon humidity, film thickness and imidization history, the diffusion coefficient and water uptake varied in the ranges of 1×10^{-9} to 3×10^{-9} $cm^2 s^{-1}$ and 0.4 to 4.5 wt%, respectively. Overall, both the diffusion coefficient and the water uptake increased with increasing humidity and film thickness, but decreased as the imidization temperature and time increased. The water sorption results were interpreted by consideration of morphological variations (molecular order, chain orientation and microvoids) due to film thickness and imidization history.

(Keywords: polyimide film; gravimetry; water diffusion)

INTRODUCTION

Water diffusion and sorption behaviour in specialty polymers is an interesting subject in both academic and industrial fields because water degrades dielectric properties and furthermore causes metal corrosion[1–4]. In particular, high-temperature aromatic polyimides are used in the fabrication of microelectronic devices as inter-dielectric, alpha-particle-protecting and passivation layers, owing to relatively high thermal stability, high chemical resistance and high mechanical toughness due to the aromatic ring and imide ring units on the chain backbone[5–8]. However, despite the relatively high chemical resistance characteristics, polyimides still absorb water, sometimes causing reliability problems in devices, such as metal corrosion and mechanical failure at interfaces[3–11].

Diffusion and sorption of water in polyimide films have previously been studied by several research groups[12–33], using quartz-spring microbalances[12–14,16,30], permeation analysers[17–20,28], electromicrobalances[15,17–22,24,29,31] capacitance analysers[21,22], quartz-crystal microbalances[23] and residual stress analysers[26,27,32]. A representative aromatic polyimide is poly(4,4′-oxydiphenylene pyromellitimide) (PMDA–ODA), which is well known as Kapton® film†. In general, PMDA–ODA film is commonly prepared from its poly(amic acid) (PAA) precursor by thermal imidization, whereas Kapton film is known to be manufactured by chemical imidization and subsequent thermal treatment. PMDA–ODA films have been extensively investigated from the viewpoint of water diffusion and sorption[12–31]. The data on water diffusion and sorption in PMDA–ODA films published previously are summarized in *Table 1*.

Yang *et al.*[12] observed that, for Kapton films, the water uptake (i.e. equilibrium water uptake) *versus* vapour pressure was concave at low vapour pressure and was upturned in the high-vapour-pressure region. This result is different from the Fickian process, in which equilibrium water uptake increases linearly with increasing vapour pressure. They interpreted the concave isotherm by dual-mode (Henry's law and Langmuir term) sorption and the upturned isotherm by Zimm–Lundberg water clustering. However, Okamoto *et al.*[16] found a sorption isotherm result slightly different from that of Yang *et al.* The water sorption increases concavely at low pressure as observed by Yang *et al.*, but increases linearly at intermediate and high vapour pressure. No sorption isotherm due to water clustering was observed. Therefore, Okamoto *et al.* concluded that the water sorption in

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† Kapton is the trademark of E. I. du Pont de Nemours & Co.

Table 1 Summary of water diffusion and sorption results of PMDA–ODA polyimide films reported previously

Film sample	Thickness (μm)	Temp. (°C)	Relative humidity (% r.h.)	Diffusion coefficient $D \times 10^{-9}$ ($cm^2 s^{-1}$)	Uptake, $M(\infty)$ (wt%)	Refs[a]
Kapton	7.6	30	100	0.8	2.73	12, 13
Kapton	50	30	100	2.6	3.12	13
Kapton	50	30	100	2.86 (3.609)	1.85	14
Kapton	50	23	100	–	2.85	15
Kapton	50	50	30–80	6.4	–	16
Kapton	117	30	100	6.5	2.9	17
Kapton	25.4	50	100	4.29	4.8	18, 19
Kapton	50.8	50	100	5.15	4.8	18, 19
Kapton	127	50	100	6.558	4.4	18, 19
Imidized at 400°C	20–60	25	75	2.6	2.50	20
Imidized at 300°C/1 h (in air) + 350°C/1 h (in N_2)	1.0, 2.6	20	100	3.8–5.6	6.0	21
Imidized in air:						
250°C/45 min	2.89	room	78	8.7	2.45	22
300°C/45 min	2.85	room	78	4.7	2.32	22
350°C/45 min	2.75	room	78	6.6	2.15	22
400°C/45 min	2.93	room	78	4.9	1.95	22
Imidized in N_2:						
400°C/1 h + 450°C/5 min	2.0	22	100	5.6	3.26	23
Imidized in N_2:						
250°C/1 h (3 h)	4.0	room	68	1.35	2.55 (2.53)	24
300°C/1 h (3 h)	4.0	room	68	1.13	2.30 (2.30)	24
350°C/1 h (3 h)	4.0	room	68	1.04	1.96 (2.00)	24
400°C/1 h (3 h)	4.0	room	68	1.03	2.04 (2.04)	24
450°C/1 h (3 h)	4.0	room	68	1.14	2.10 (2.30)	24
Imidized in N_2:						
400°C/1 h	10	25	50	1.68	–	25, 26
Imidized in air:						
350°C/30 min	6.7	room	100	4.9	–	27
350°C/30 min	11.4	room	100	5.2	–	27
350°C/30 min	18.7	room	100	4.9	–	27
350°C/30 min	19.2	room	100	5.5	–	27
350°C/30 min	27.3	room	100	5.6	–	27
Imidized in N_2:						
40°C/1 h	8.9–9.5	23	75	0.98–2.27	1.65–2.27	15
	15.1–19.9	23	75	1.30–2.49	1.68–2.18	15
	29.1	23	75	1.02	1.67	15
Imidized in vacuum:						
200°C/10 h	100	50	60–80	16.6	–	16

[a] Refs. 17, 18, 19 and 20: measured using permeation techniques
Refs. 15, 17, 18, 19, 20, 21, 22 and 24: measured using electromicrobalances (Cahn, Mettler, and other microbalances)
Refs. 12, 13, 14 and 16: measured using quartz-spring microbalances
Ref. 23: measured using a quartz-crystal microbalance
Refs. 21 and 22: measured by capacitance measurement techniques
Refs. 25, 26 and 27: measured using film stress relaxation techniques

Kapton film occurs in the dual mode, but does not differ much from the Henry's law isotherm. The same conclusion was reached by Yang *et al.* in their extended study[14]. In addition, they found that the water sorption in Kapton films follow well a Fickian law at low water vapour pressure and short exposure times. Recently, Lim *et al.*[15] have also found that the water sorption in Kapton films follows a Fickian law with a small departure at longer sorption times. However, Hubbell *et al.*[17] and Sacher *et al.*[18] have reported that the water uptake increases

linearly with increasing vapour pressure or percentage relative humidity (% r.h.), indicating that the water sorption in Kapton films obey Henry's law and Fick's second law. From these results, it is conclusively suggested that in Kapton films the water diffusion and sorption apparently obey Fick's second law within a very small deviation.

The dependence of water uptake on temperature was also studied by Yang *et al.*[12] and Sacher *et al.*[18]. Yang *et al.* found that water uptake decreases with increasing temperature. In contrast, Sacher *et al.* observed that the water uptake at 100% r.h. does not depend upon temperature over the range 30–85°C. A detailed investigation is needed to clarify this situation.

Unlike the temperature dependence of water uptake, the diffusion coefficient of water in Kapton films always increases with increasing temperature. However, the dependence of diffusion coefficient on water vapour pressure (% r.h.) is not consistent between research groups. Hubbell *et al.*[17] found that the diffusion coefficient increases with vapour pressure. In contrast, Yang *et al.*[12] found that the diffusion coefficient of water increases with vapour pressure at low vapour pressure, but that this turns to a decrease in the high-vapour-pressure region. A similar result was obtained by Sacher *et al.*[18]. However, in the study of Okamoto *et al.*[16] the diffusion coefficient increases with vapour pressure at low vapour pressure and levels off at intermediate and high vapour pressure. For this matter, again, a detailed investigation is also needed.

Another interesting subject in water diffusion and sorption is the effect of film thickness. According to the study of Yang *et al.*[14], the diffusion coefficient was higher in thick films than in thin films. This result is in good agreement with that reported by Sacher *et al.*[18]. However, there is no agreement on water uptake *versus* film thickness. Yang *et al.*[12] have observed that water uptake was higher in thin films than in thick films at low vapour pressure, but vice versa at high vapour pressure. In contrast, Sacher *et al.*[18] have found that water uptake is independent of film thickness.

The study of water diffusion and sorption was extended to PMDA–ODA films thermally imidized from the poly(amic acid) precursor by several research groups[15,16,20–27]. Water diffusion in thermally imidized films occurs by a Fickian process[21–27] or a nearly Fickian process[15,16] as observed in Kapton films, regardless of imidization temperature over the range 200–450°C. However, both diffusion coefficient and water uptake are functions of thermal imidization history. Denton *et al.*[22] found that, for films, except the film imidized at 300°C, both diffusion coefficient and water uptake decreased linearly with increasing imidization temperature (see *Table 1*). These results were obtained for films thermally imidized in air. They extended the same type of measurements to films thermally imidized in a nitrogen atmosphere[24]. Both water diffusion coefficient and equilibrium water sorption are functions of imidization temperature over the range 250–450°C; however, they show a minimum diffusion coefficient between 350 and 400°C (see *Table 1*). A similar result was previously reported by Wilson *et al.*[33]. The increase in water sorption and diffusion coefficient for films imidized at $\geqslant$400°C is attributed to partial thermo-oxidative degradation of the polyimide. They estimated that, for all the films, the equilibrium water uptake at 100% r.h. was 3–4 wt%, higher than 1.96–2.55 wt% at 68% r.h. In comparison with the films imidized thermally in air, the films imidized in the nitrogen atmosphere exhibited lower diffusion coefficients and comparable water uptakes.

Lim *et al.*[15] and Jou *et al.*[27] have investigated thermally imidized films of 6.7–29.1 μm thickness. They found apparently no effect of film thickness on the diffusion coefficient and water uptake within a small variation over the limited range of film thickness, except that the diffusion coefficients measured by Jou *et al.* are relatively higher than those reported by Lim *et al.*

As reviewed above, several questions remain to be answered in spite of numerous studies performed on water solubility in PMDA–ODA films, including Kapton films (chemically imidized and followed by heat treatment) and thermally imidized films: (i) the effect of temperature on water uptake; (ii) the effect of vapour pressure (or relative humidity) on diffusion coefficient; and (iii) the effect of film thickness on water uptake. Beyond these questions, the relationship of water sorption to film morphology (molecular chain order, packing and orientation) has not yet been fully understood. Furthermore, the values of diffusion coefficient and water uptake are quite scattered, depending on film samples (even though produced by a single manufacturer or prepared by the same method), measurement techniques and research groups, as shown in *Table 1*.

In this study, PMDA–ODA films were prepared from the poly(amic acid) by thermal imidization at various temperatures in the range 230–400°C as shown in *Figure 1*. The thickness of the films was in the range of 10–110 μm. Molecular order and orientation in the films were characterized by wide-angle X-ray diffraction (WAXD) and prism coupling analysis. The water sorption

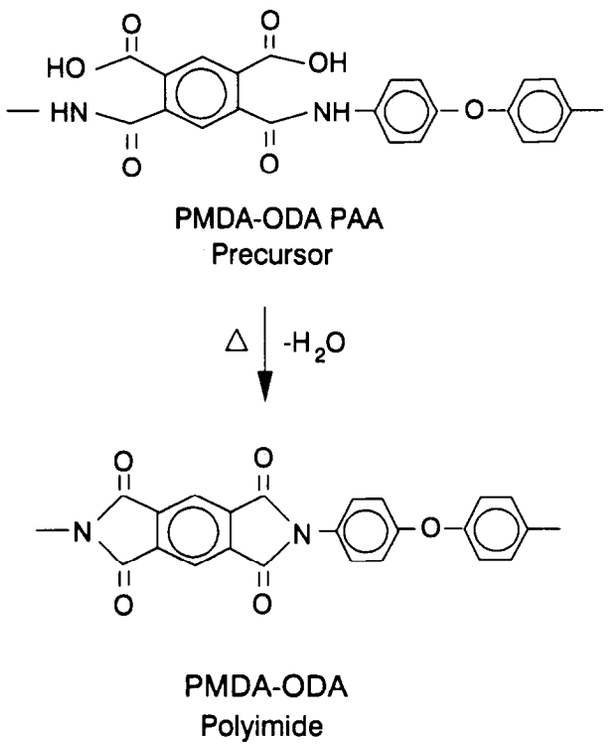

Figure 1 Poly(4,4′-oxydiphenylene pyromellitimide) (PMDA–ODA) imidized thermally from the poly(amic acid) precursor

Table 2 Thermal imidization schedules employed in the preparation of PMDA–ODA polyimide films

Thermal imidization process	Imidization schedule with 2.0 K min^{-1} ramping rate per step
230°C/2 h	150°C/30 min + 230°C/2 h
230°C/10 h	150°C/30 min + 230°C/10 h
300°C/1 h	150°C/30 min + 230°C/30 min + 300°C/1 h
300°C/10 h	150°C/30 min + 230°C/30 min + 300°C/10 h
350°C/1 h	150°C/30 min + 230°C/30 min + 300°C/30 min + 350°C/1 h
350°C/10 h	150°C/30 min + 230°C/30 min + 300°C/30 min + 350°C/10 h
400°C/1 h	150°C/30 min + 230°C/30 min + 300°C/30 min + 400°C/1 h
400°C/1–4 h	150°C/30 min + 230°C/30 min + 300°C/30 min + 400°C/1–4 h
400°C/10 h	150°C/30 min + 230°C/30 min + 300°C/30 min + 400°C/10 h

behaviour was investigated in detail by gravimetry using a Cahn microbalance. The water sorption behaviour was understood together with relative humidity, film thickness thermal imidization history and morphological structure.

EXPERIMENTAL

Materials and sample preparation

Poly(4,4′-oxydiphenylene pyromellitamic acid) (PMDA–ODA PAA) precursor (ca. 35 000 $\bar{M}_w$ and 16 wt% solid content) solutions in *N*-methyl-2-pyrrolidinone (NMP) were used in this study as received from Du Pont Chemical Co. The precursor solutions were spin-cast on silicon wafers, which were precleaned for 5 min in an oxygen plasma asher operated at 150 W, followed by drying in a convection oven at 85°C for 30 min. Dried precursor films were thermally imidized at various temperatures of 230–400°C under a nitrogen gas flow. The imidization time was 1–10 h at the chosen imidization temperature. The heating and cooling rates employed were 2.0 and 1.0 K min^{-1}, respectively. The detailed imidization protocols employed are summarized in *Table 2*. The thickness of the imidized films was ca. 13 μm. Here, the film thickness was measured using an alpha-stepper of Tencor Instruments Co. In the case of $>30\,\mu$m thick films, the process of spin-coating and softbaking was repeated several times before imidization, depending on the final film thickness desired. The final softbaked films were thermally imidized at 400°C for 1–4 h, depending on the film thickness: the longer time was given to the thicker films. The thickness of the films, which was used to study the film thickness dependence of water sorption, was 10–110 μm. After thickness measurements, the films were taken off from the substrates with the aid of deionized water, and dried for 2 days at 100°C in a vacuum oven at 5×10^{-4} Torr. For measurements of water sorption, films were cut to a size of 12 mm × 15 mm using a blade, and fully dried in a high vacuum of 2×10^{-6} Torr for 2–3 days before use. In addition, for X-ray diffraction measurements, films were diced to a dimension of 15 mm × 15 mm, and the film strips were stacked together to a total thickness of 110–150 μm.

Measurements

For the polyimide films, water diffusion and uptake were measured at 22–100% relative humidity (r.h.) at 25°C as a function of time, using an electromicrobalance (Cahn Instruments, model 2000) with a resolution of 1 μg over $\leqslant$20 mg weight loading (see *Figure 2*). Here, the relative humidities of 22–100% were obtained using distilled water (23.76 mmHg vapour pressure = 100% r.h.) and saturated solutions of various salts, namely 74.4 wt% KCl (20.19 mmHg vapour pressure = 85% r.h.), 73.7 wt% NaCl (17.89 mmHg vapour pressure = 75% r.h.), 27.0 wt% $Ca(NO_3)_2\cdot4H_2O$ (11.64 mmHg vapour pressure = 49% r.h.) and 28.0 wt% $K(OOCCH_3)\cdot1.5H_2O$ solutions (5.35 mmHg vapour pressure = 22% r.h.)[34]. Wide-angle X-ray diffraction (WAXD) measurements were conducted on a Rigaku powder diffractometer (model D/MAX-B) with a rotating-anode X-ray generator (model RU200B). The CuKα radiation source was operated at 40 kV and 40 mA. Step and scan data were taken in the $\theta/2\theta$ mode under computer control at 0.02° (2θ) intervals with a scan speed of 0.4–1.0° min^{-1}, depending upon whether a reflection or transmission scan was being made. Diffractograms were collected over 3–60° (2θ) with the diffraction vector both normal to and in the plane of the films. 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). In addition, the refractive indices were measured at room temperature using a prism coupler (model 2010 of Metricon Co.) equipped with a He–Ne laser light source of 632.8 nm wavelength. The in-plane and out-of-plane refractive indices (n_{xy} and n_z) were measured in transverse electric and transverse magnetic mode, respectively, by choosing the appropriate polarization of the incident laser light. The film birefringence (Δ) was estimated from the refractive indices: $\Delta = n_{xy} - n_z$.

RESULTS AND DISCUSSION

Analysis of water sorption isotherms

The water sorption in thermally imidized PMDA–ODA films was measured at 25°C as a function of time,

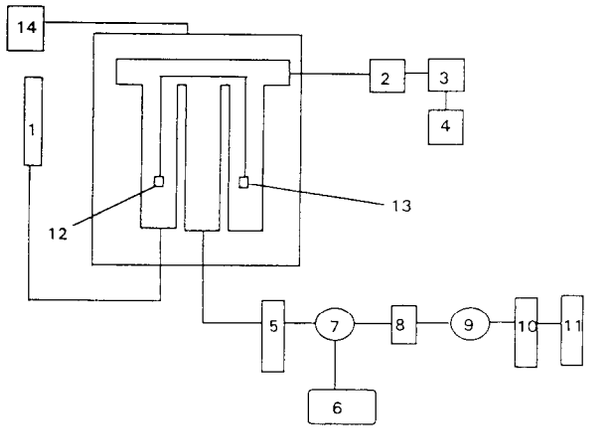

Figure 2 Schematic diagram of Cahn microbalance used in the present study: 1, reservoir; 2, balance controller; 3, digital multimeter; 4, chart recorder; 5, vacuum trap; 6, vacuum pump; 7, control valve; 8, rotameter; 9, regulator; 10, drier chamber; 11, nitrogen gas tank; 12, sample; 13, reference weight; 14, temperature controller

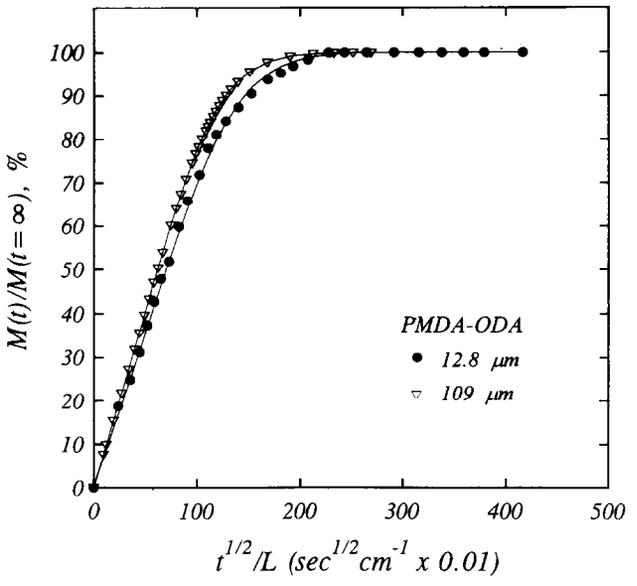

Figure 3 Water sorption isotherms of PMD–ODA films measured at 25°C and 100% r.h. The polyimide films were prepared by imidization at 400°C

Table 3 Variations of water diffusion coefficient and sorption with relative humidity in PMDA–ODA films[a]

Relative humidity (% r.h.)	Diffusion coefficient, $D \times 10^{-9}$ ($cm^2 s^{-1}$)	Water uptake, $M(\infty)$(wt%)
22	1.00	0.4
49	1.12	1.4
75	1.04	2.3
85	1.10	2.8
100	1.04	3.4

[a] Films were prepared by thermal imidization at 400°C and their thickness was 45.7 μm. Water sorption measurements were performed at 25°C

humidity, film thickness and thermal history. Typical water sorption isotherms are shown in *Figure 3*. The sorption isotherms of all the polyimide films were reasonably well fitted by Fick's second law, regardless of humidity, film thickness and imidization history. However, some of the film samples showed a Fickian water diffusion process with a small departure (see the sorption isotherm of the 12.8 μm thick film in *Figure 3*). Overall, the water sorption in all the PMDA–ODA films apparently follows well Fick's law. This is consistent with the results[14–19,21–24] reported previously. Therefore, all the sorption isotherms measured were analysed with equation (1) below, which is the typical solution to Fick's second law[35], giving the diffusion coefficient of water:

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

where $M(t)$ is the water uptake at time t, $M(\infty)$ is the water uptake at $t = \infty$, D is the diffusion coefficient of water and L is the film thickness.

In fact, PMDA–ODA polyimide molecules in films at room temperature are in the solid state with two phases, ordered and disordered (or less ordered) phases[36–38]. Thus, from the morphology, one should expect that the water diffusion in the ordered phase is different from that in the less ordered phase, resulting in some deviations from the typical Fickian type of water diffusion derived under the assumption that the films are homogeneous. However, the results measured in this study apparently obey Fick's second law in spite of the morphological heterogeneity in the polymer films. In general, water diffusion in a polymer is confined to the less ordered phase since water diffusion in the ordered phase is relatively very slow even if water molecules penetrate and diffuse through the ordered state. Thus, the overall diffusion of water in PMDA–ODA films may depend upon the degree of crystallinity as well as the morphological organization.

Effect of humidity

In order to investigate the effect of humidity (i.e. vapour pressure) on diffusion coefficient and sorption, a film of 45.7 μm thickness imidized at 400°C was selected. Water sorption measurements were performed at 25°C over the range of 22–100% r.h. The results are shown in *Table 3* and *Figures 4* and *5*. The diffusion coefficient varied slightly with humidity in the range of 1.00×10^{-9} to 1.12×10^{-9} $cm^2 s^{-1}$. Apparently, the diffusion coefficient is invariant with humidity within experimental error. This indicates that the water diffusion in the PMDA–ODA film apparently obeys Fick's second law. This is not consistent with the results[12,16–18] reported previously.

The effect of humidity was more clear on the water uptake behaviour in the films. The water uptake increased with increasing relative humidity from 0.4 wt% in 22% r.h. to 3.4 wt% in 100% r.h. (see *Table 3* and *Figure 5*). The water uptake *versus* relative humidity plot is almost linear over 22–100% r.h., but is not totally linear over the whole range of 0–100% r.h. This result is evidence that the water sorption process in the PMDA–ODA films is not truly Fickian, that is, it departs slightly from the Fickian process. However, the polyimide film did not

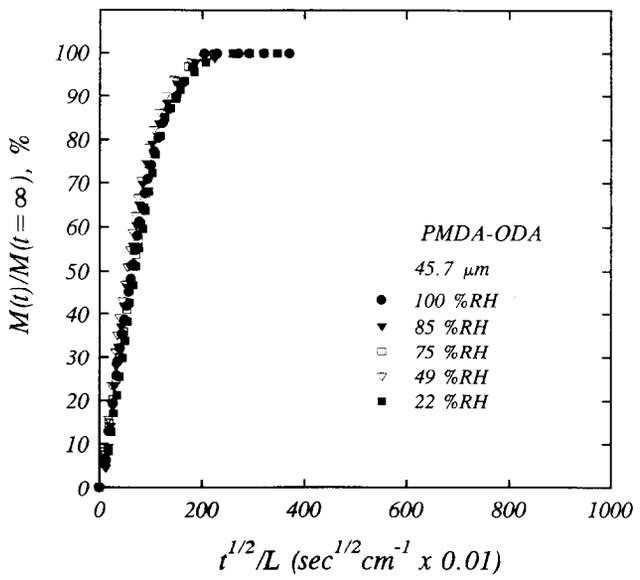

Figure 4 Water sorption isotherms of a 45.7 μm thick PMDA–ODA film measured at 25°C and various relative humidities. The polyimide film was imidized at 400°C

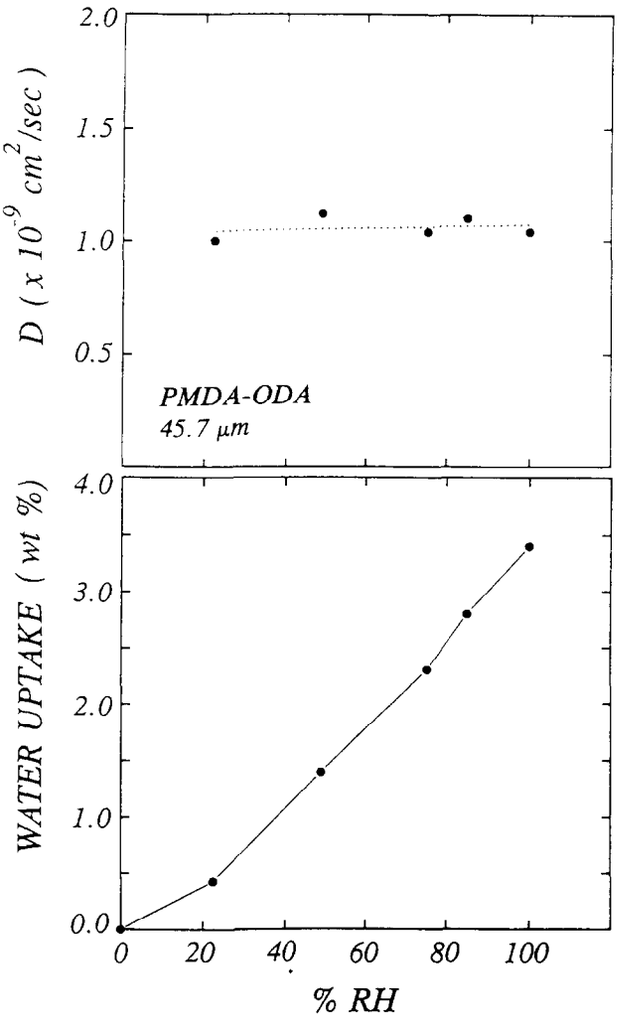

Figure 5 The effect of humidity on the diffusion coefficient and water uptake in a 45.7 μm thick PMDA–ODA film measured at 25°C

show a water uptake curve that was concave towards the r.h. axis, which is characteristic of dual-mode sorption. Instead, the water uptake curve was slightly upturned in the range of 0–49% r.h. Therefore, we speculate that the small departure from the Fickian process in the sorption behaviour may be due to water clustering or water plasticization rather than to dual-mode sorption. However, a detailed study is needed to clarify the origin of the small deviation from the Fickian process.

Effect of thermal imidization history

According to a previous thermal imidization study of poly(amic acid) precursors by *FT*i.r. and t.g.a.–mass spectroscopy[39], in the case of thin polyimide films with $<25\,\mu m$ thickness, poly(amic acid) precursors were completely converted to the polyimide by thermal imidization above 230°C, and also residual solvent was completely removed from the resulting polyimide film. Thus, the polyimide films used in this study were prepared by various thermal imidization processes over the range of 230–400°C (see *Table 2*). The thickness of the films was controlled in the range of 12.4–13.3 μm to minimize the effect of film thickness. The sorption isotherms, which were measured at 25°C and 100% r.h., are illustrated in *Figure 6*. The diffusion coefficient and water uptake obtained are presented in *Table 4* and *Figure 7*. For films imidized for 1 h, the diffusion coefficient and water uptake decreased with increasing imidization temperature from $3.00\times10^{-9}\,cm^2\,s^{-1}$ and 4.5 wt% for the film imidized at 230°C to $1.20\times10^{-9}\,cm^2\,s^{-1}$ and 2.5 wt% for the film imidized at 400°C, respectively. On the other hand, for films imidized for 10 h, the diffusion coefficient and water uptake also decreased from $2.70\times10^{-9}\,cm^{-2}\,s^{-1}$ and 4.2 wt% for the 230°C imidized film to $1.10\times10^{-9}\,cm^2\,s^{-1}$ and 2.3 wt% for the 400°C imidized film, respectively. In comparison, for the films imidized at a given temperature, the film imidized for 10 h showed a lower diffusion coefficient and water uptake than did the film imidized for 1 h, indicating that thermal annealing further lowers the water diffusion coefficient and sorption in PMDA–ODA films. Overall, both diffusion coefficient and water uptake are decreasing functions of imidization temperature and time (i.e. thermal annealing time). In addition, it is noted here that, as shown in *Figure 7*, the diffusion coefficient *versus* temperature plot did not show a minimum over the range 300–400°C, which was reported previously by Denton *et al.*[22,24]. According to their results, the diffusion coefficient and water uptake varied a

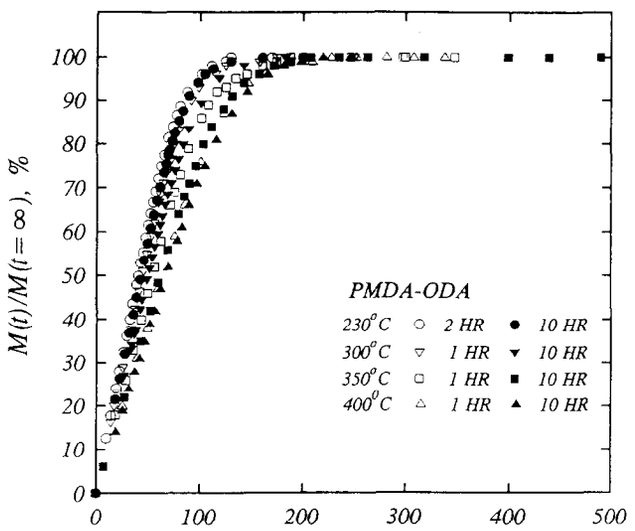

Figure 6 Water sorption isotherms of PMDA–ODA films imidized at 230–400°C for 1–10 h. The measurement was performed at 25°C and 100% r.h.

Table 4 Water diffusion coefficient and sorption of PMDA–ODA films prepared by various imidization processes[a]

Thermal imidization process	Film thickness (μm)	Diffusion coefficient, $D\times10^{-9}$ ($cm^2\,s^{-1}$)	Water uptake, $M(\infty)$(wt%)
230°C/2 h	13.2	3.00	4.5
230°C/10 h	13.1	2.70	4.2
300°C/1 h	13.2	2.50	4.1
300°C/10 h	13.0	2.00	3.8
350°C/1 h	12.9	1.70	3.7
350°C/10 h	13.3	1.30	3.1
400°C/1 h	12.4	1.20	2.5
400°C/10 h	12.7	1.10	2.3

[a] Water sorption measurements were performed at 25°C and 100% r.h.

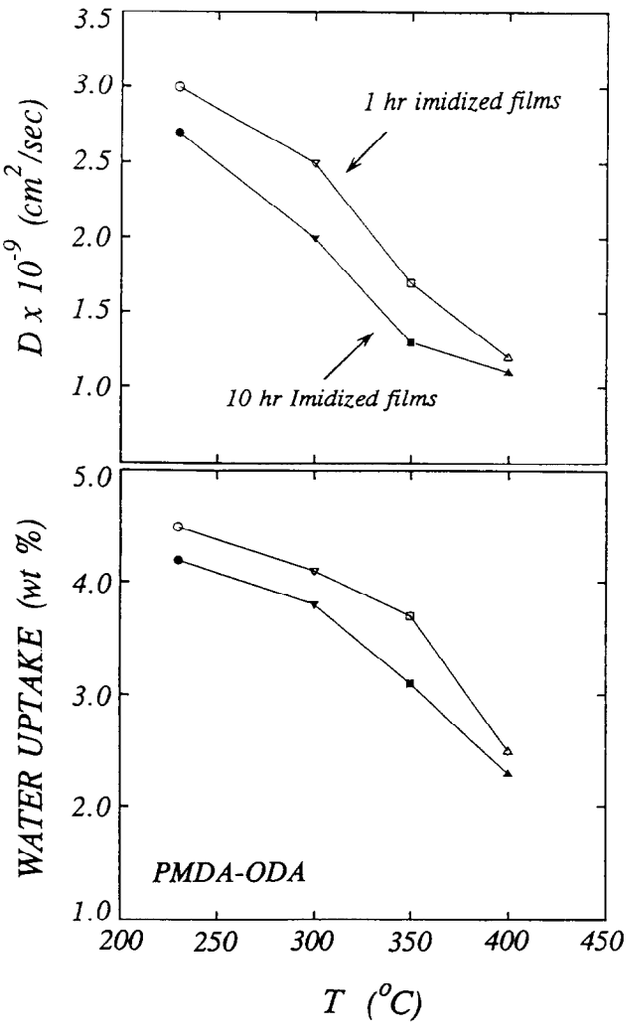

Figure 7 The effect of thermal imidization history on the diffusion coefficient and water uptake in PMDA–ODA films imidized at 230–400°C for 1–10 h. The measurement was performed at 25°C and 100% r.h.

very little in the ranges 1.03×10^{-9} to 1.35×10^{-9} $cm^2 s^{-1}$ and 1.96 to 2.55 wt%, respectively. The variations with thermal imidization history are relatively small compared to those observed in the present study, although our results could not be exactly compared to their results because of the different film thickness and vapour pressure employed.

The water sorption behaviour observed can be understood by consideration of morphological variations with imidization history. For this, WAXD measurements were performed for the polyimide films in both transmission and reflection geometry. The results are presented in *Figure 8*. All the transmission X-ray diffraction patterns, which give structural information in the film plane, showed two distinct peaks, one at $2\theta < 9°$ and the other at $9° < 2\theta < 40°$: the single sharp diffraction peak in the low-angle region results from the polymer chain ordered along the chain axis, whereas the broad peak is due to the diffraction of a poor intermolecular packing combined with the amorphous halo[38,40]. However, the intensity and shape of these peaks depend upon the thermal imidization history. As the imidization temperature and time increase, the low-angle diffraction peak becomes significantly strong and sharp, whereas the diffraction peak in the region of 9–40° (2θ) improves slightly but is still relatively broad. For the low-angle peak, the *d*-spacing, which corresponds to the projected length of the chemical repeat unit ordered along the chain axis, increased from 15.31 Å for the film imidized at 230°C for 1 h to 15.77 Å for the film imidized at 400°C for 10 h, whereas the coherence length (L_c), which was calculated with an instrumental broadening of 0.15° (2θ) from the Scherrer relationship[41], increased from 62 Å for the film imidized at 230°C for 1 h to 74 Å for the film imidized at 400°C for 10 h. The mean intermolecular distance, which was estimated from the maximum of the broad peak at $9° < 2\theta < 40°$, decreased slightly from 5.24 Å for the film imidized at 230°C for 1 h to 5.07 Å for the film imidized at 400°C for 10 h.

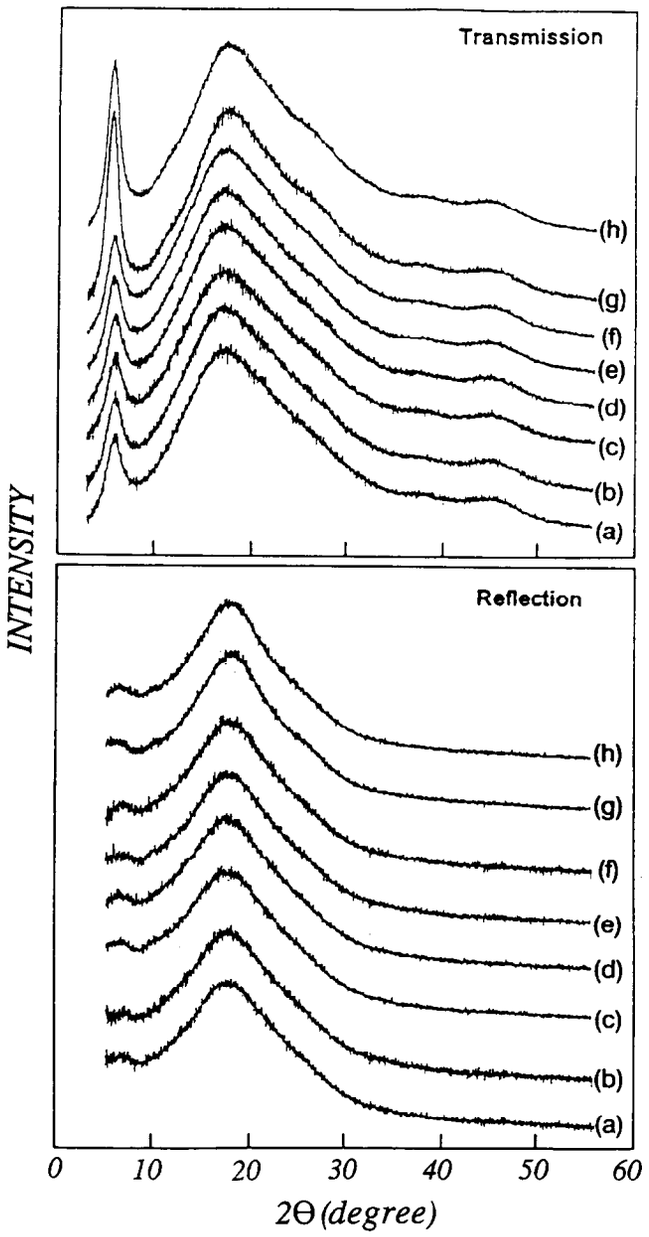

Figure 8 Wide-angle X-ray diffraction patterns of PMDA–ODA films imidized at 230–400°C for 1–10 h: (a) 230°C/2 h; (b) 230°C/10 h; (c) 300°C/1 h; (d) 300°C/10 h; (e) 350°C/1 h; (f) 350°C/10 h; (g) 400°C/1 h; (h) 400°C/10 h. The measurement was performed with a Cu Kα radiation source at room temperature

Table 5 Refractive indices and birefringence of PMDA–ODA films prepared by various imidization processes[a]

Thermal imidization process	Film thickness (μm)	Refractive index		Birefringence, Δ
		n_{xy}	n_z	
230°C/2 h	13.2	1.7091	1.6367	0.0724
230°C/10 h	13.1	1.7108	1.6361	0.0747
300°C/1 h	13.2	1.7116	1.6368	0.0748
300°C/10 h	13.0	1.7118	1.6367	0.0751
350°C/1 h	12.9	1.7128	1.6367	0.0761
350°C/10 h	13.3	1.7138	1.6380	0.0758
400°C/1 h	12.4	1.7242	1.6414	0.0828
400°C/10 h	12.7	1.7252	1.6446	0.0806

[a] Refractive indices were measured at 632.8 nm

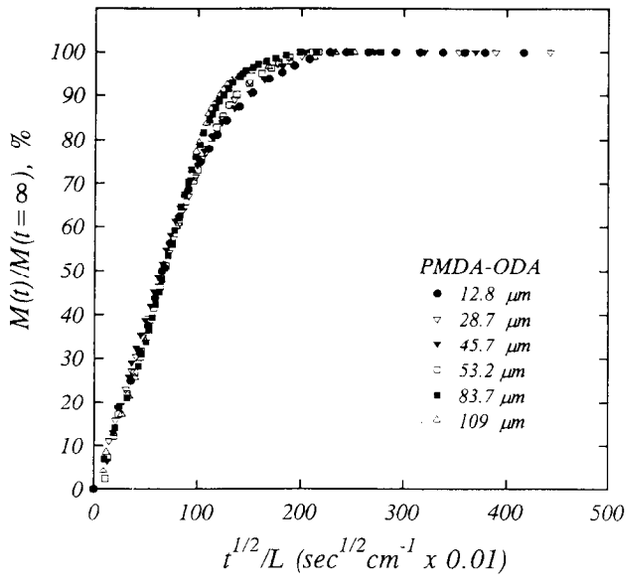

Figure 9 Water sorption isotherms of PMDA–ODA films with various film thicknesses measured at 25°C and 100% r.h. All the polyimide films were imidized at 400°C

The reflection X-ray diffraction patterns, which give structural information in the out-of-film plane, showed a broad peak at $10° < 2\theta < 40°$ and a very weak, broad peak at $< 10°$ (2θ), regardless of thermal imidization history. However, the broad peak at $10° < 2\theta < 40°$ is slightly sharpened as the imidization temperature and time increase. The mean intermolecular distance, which was estimated from the peak maximum, decreased slightly from 5.11 Å for the film imidized at 230°C for 1 h to 5.03 Å for the film imidized at 400°C for 10 h. On comparison of the reflection pattern with the transmission pattern, it can be deduced that the polymer chains are mostly aligned in the film plane rather than randomly, and are more closely packed in the out-of-film plane than in the film plane. Here, the degree of molecular in-plane orientation was enhanced by imidization at higher temperature for longer time (see the transmission patterns). The molecular in-plane orientation was further confirmed by the film refractive indices and birefringence measurements. As presented in *Table 5*, the in-plane refractive index was always higher than the out-of-plane refractive index, indicating that the polymer chains are preferentially aligned in the film plane. The film birefringence (Δ), which is a measure of molecular in-plane orientation[42], increased as the imidization temperature and time increased.

Therefore, the lower diffusion coefficient and water sorption in a film imidized at higher temperature for longer time result mainly from morphological changes, such as the enhancement of polymer chain order, molecular in-plane orientation and intermolecular packing. In addition, it is noted here that the water diffusion process may be anisotropic in the film plane and in the out-of-film plane because of the anisotropic molecular packing due to the high degree of molecular in-plane orientation. Furthermore, the dimension of the film samples used was 12 mm × 15 mm in the film plane and ca. 13 μm thickness: the pathway of water molecules being moved is much longer in the film plane than in the out-of-film plane. Thus, the diffusion of water molecules into the film might occur predominantly in the direction perpendicular to the film plane.

Effect of film thickness

Water sorption measurements were performed at 25°C and 100% r.h. for polyimide films imidized at 400°C for 1–4 h (see *Figures 9* and *10* and *Table 6*). The diffusion coefficient varied very little in the range 1.00×10^{-9} to

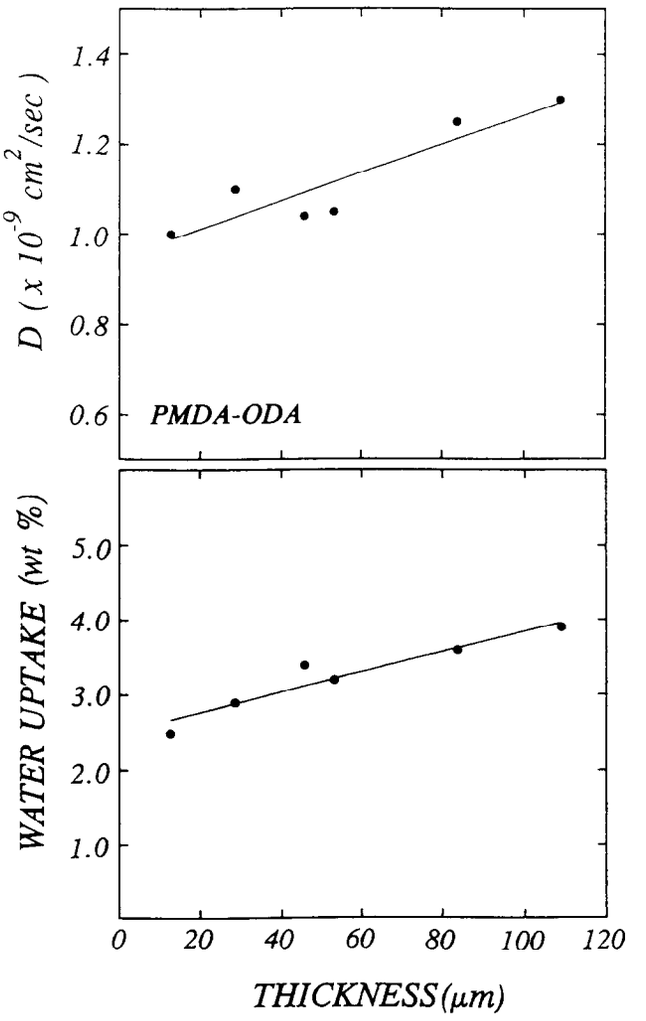

Figure 10 The effect of film thickness on the diffusion coefficient and water uptake in PMDA–ODA films with various film thicknesses measured at 25°C and 100% r.h. All the polyimide films were imidized at 400°C

Table 6 Variations of water diffusion coefficient and sorption with film thickness in PMDA–ODA films[a]

Film thickness (μm)	Diffusion coefficient, $D \times 10^{-9}$ ($cm^2 s^{-1}$)	Water uptake, $M(\infty)$(wt%)
12.8	1.00	2.5
28.7	1.10	2.9
45.7	1.04	3.4
53.2	1.05	3.2
83.7	1.25	3.6
109	1.30	3.9

[a] Films were prepared by thermal imidization at 400°C. Water sorption measurements were performed at 25°C and 100% r.h.

Table 7 Refractive indices and birefringence of PMDA–ODA films with various thicknesses[a]

Film thickness (μm)	Refractive index		Birefringence, Δ
	n_{xy}	n_z	
12.8	1.7279	1.6426	0.0853
28.7	1.7277	1.6471	0.0806
45.7	1.7277	1.6477	0.0800
53.2	1.7277	1.6378	0.0799
83.7	1.7277	1.6480	0.0797
109	1.7270	1.6485	0.0785

[a] Films were prepared by thermal imidization at 400°C. Refractive indices were measured at 632.8 nm

1.10×10^{-9} $cm^2 s^{-1}$ over the thickness range of 12.8–53.2 μm, and increased with increasing thickness over the range of $\geqslant 53.2$ μm. That is, within an error, the diffusion coefficient apparently increases linearly with film thickness. Similar studies were previously conducted for Kapton films by Yang *et al.*[14] and Sacher *et al.*[18]. They found that the diffusion coefficient of water in Kapton films is higher in thick films than in thin films. Therefore, the result in this study is in agreement with their results, although the film samples were prepared in different ways, chemical imidization followed by machine-drawing in a heating zone *versus* thermal imidization.

The water uptake increased almost linearly with film thickness for 2.5 wt% for the 12.8 μm thick film to 3.9 wt% for the 109 μm thick film. Yang *et al.*[14] and Sacher *et al.*[18] previously studied the water uptake *versus* film thickness behaviour in Kapton films. Sacher *et al.*[18] found that water uptake is not a function of film thickness. In contrast, Yang *et al.*[14] found that water uptake is a function of film thickness as well as water vapour pressure. The water uptake decreased with increasing film thickness in the low-vapour-pressure region, but increased with film thickness in the high-vapour-pressure region. In our study, the measurement of water uptake was conducted in only 100% r.h., a high vapour pressure. With the limited database, the film thickness dependence of water uptake observed in this study is in agreement with the result of Yang *et al.*, which was measured in the high-vapour-pressure region. However, the humidity effect on water diffusion and uptake was discussed earlier: water uptake increases with increasing relative humidity for a film of a given thickness. Based on this result, the water uptake–film thickness behaviour with varying vapour pressure is not fully understood. We speculate that the water uptake increases with increasing film thickness at any given vapour pressure.

The film thickness dependence of water diffusion coefficient and uptake might result from morphological changes due to the variation of film thickness. Here, the morphological factors in the polymer film that may be considered are polymer chain order, chain orientation, intermolecular packing and presence of microvoids. In this study, all the films were prepared by spin-coating of the poly(amic acid) solution on silicon crystal substrates, followed by drying at 85°C and thermal imidization at 400°C. In this case, during the thermal drying and imidization, shrinking of spin-cast precursor films occurs only in the direction perpendicular to the film plane, leading to the in-plane orientation of polymer chains[42]. The degree of molecular in-plane orientation generally increases with decreasing film thickness[42]. In the present study, the film birefringence, which is a measure of molecular in-plane orientation, was estimated from the film refractive indices measured as a function of film thickness (see *Table 7*). The in-plane refractive index (n_{xy}) was always higher than the out-of-plane refractive index (n_z), regardless of the film thickness over the range of 12–109 μm. However, with increasing film thickness, n_{xy} decreased slightly and, in contrast, n_z increased slightly, resulting in film birefringence. The birefringence decreased with increasing film thickness from 0.0853 to 0.0785 over the thickness range considered, indicating that molecular in-plane orientation is a decreasing function of film thickness. This variation of molecular in-plane orientation with film thickness may affect the intermolecular packing and the order of the polymer chain itself in the films. On the other hand, during thermal imidization of the dried poly(amic acid) precursor films, water molecules (the imidization by-product) and residual NMP molecules are degassed, perhaps creating microvoids in the resulting film. The trend to generate microvoids may increase with increasing film thickness. Therefore, the higher diffusion coefficient and water uptake in thicker films might result from both the microvoids generated by outgassing of water by-product and residual NMP and the increase in free volume due to the decrease in chain order and in-plane orientation.

CONCLUSIONS

The water sorption behaviour of PMDA–ODA films, which were thermally imidized from the poly(amic acid) precursor solution under various conditions, were gravimetrically investigated as a function of relative humidity, film thickness and imidization history. In addition, the film morphology was characterized by X-ray diffraction and prism coupling analysis. Water diffusion in the polyimide films followed a nearly Fickian process, which showed a very small departure from Fick's second law, regardless of humidity, film thickness, imidization history and morphological heterogeneity (ordered and less ordered phases). Depending upon the humidity, film thickness and imidization history, the diffusion coefficient and water uptake varied in the ranges of 1×10^{-9} to 3×10^{-9} $cm^2 s^{-1}$ and 0.4 to 4.5 wt%, respectively. Both the diffusion coefficient and the water uptake increased with increasing humidity and film thickness, and decreased as the imidization temperature and time

increased. This water sorption behaviour might result from the morphological variations in the film, such as polymer chain order and orientation, intermolecular packing and microvoids, due to the film thickness and imidization history. The higher imidization temperature and longer imidization time gave higher chain order, in-plane orientation and intermolecular packing, leading to decreases in both diffusion coefficient and water uptake. As film thickness increases, both the decrease in chain order and in-plane orientation and the formation of microvoids due to water by-product and residual solvent might occur favourably, consequently leading to the increase in both diffusion coefficient and water uptake.

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