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Water sorption and diffusion behaviours in thin films of photosensitive polyimides

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Several photosensitive polyimide (PSPI) precursors were synthesised by the acid/base complexations of conventional poly(amic acid) precursors with photochemically cross-linkable 2-(dimethylamino)ethyl methacrylate. PSPIs in films were prepared from the photosensitive precursors by thermal imidisation, whereas the corresponding PIs in films were prepared from the conventional poly(amic acid)s: rod-like poly(p-phenylene pyromellitimide) (PMDA-PDA), rigid poly(p-phenylene biphenyltetracarboximide) (BPDA-PDA), semi-flexible poly(4,4′-oxydiphenylene biphenyltetracarboximide) (BPDA-ODA), semi-flexible poly(4,4′-oxydiphenylene pyromellit-imide) (PMDA-ODA), and flexible poly(4,4′-oxydiphenylene benzophenonetetracarboximide) (BTDA-ODA). Water sorption and diffusion behaviours in the PSPIs were gravimetrically measured at 25°C in 100% relative humidity and compared with those of the corresponding PIs. For the PSPIs as well as the PIs, the water sorption and diffusion behaviours were nearly Fickian, regardless of the backbone chemistry. However, those were strongly dependent upon the polyimide backbone chemistry and precursor origin. In addition, those in polyimides were affected by the bulky photosenistive groups, even though they were temporarily linked to the precursor polymers and then debonded from the backbones and ultimately outgassed during the thermal imidisation process. For PMDA-PDA, BPDA-PDA and BPDA-ODA, the PSPIs absorbed water more quickly than the corresponding PIs, whereas for PMDA-ODA and BTDA-ODA, the PSPIs absorbed water less quickly than the corresponding PIs. In contrast to the water diffusion, all the PSPIs absorbed slightly more or a great deal more water than the corresponding PIs, depending on the backbone chemistry. All the measured water sorption and diffusion behaviours in the PSPIs were understood by considering changes in the morphological structure (namely, chain order and orientation), voids, and residues possibly induced by the bulky photosensitive groups, in addition to the T_g as well as the chemical affinity to water. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: photosensitive polyimide; conventional polyimide; thermal imidisation)

INTRODUCTION

Recently, photosensitive polyimides (PSPIs) have gained great attention in the microelectronics industry, owing to the simple fabrication process due to their direct patternability, in addition to the high thermal stability, excellent mechanical properties, good dielectric properties, and high chemical resistance[1–9]. PSPIs are classified into inherently photosensitive polyimides (preimidised PSPIs)[3–5] and polyimide precursors functionalised with photoactive groups (PSPI precursors)[1,2,6–9]. They are photoactive to ultraviolet (u.v.) light negatively or positively[1–9]. Preimidised PSPIs are limited to the flexible, soluble polyimides because of the solubility requirement in organic solvents, whereas PSPI precursors do not have any limitation in the backbone chemistry because of the inherently high solubility in solvents. Sometimes, these PSPIs are further formulated with photopackage components, including photosensitisers and photo-cross-linkable monomers, in order to enhance their lithographic performance.

PSPIs have been mostly studied in the aspect of lithographic performance[1–4,6–8], however, their structure and properties have been rarely investigated[5,9–11]. In the case of preimidised PSPIs, they become cross-linked polymers through the reaction of the photoactive groups by photoexposure, so that the crosslinked photoactive groups permanently remain in the resulting polymers[3,4]. The cross-linkages permanently remained in the PSPIs may affect the morphological structure and properties. According to a previous study on a preimidised PSPI system[5], dynamic and static mechanical properties were varied with the variation of the energy dose exposed by UV light, indicating that the photochemically generated cross-links affected the mechanical properties.

On the other hand, for PSPI precursors, photosensitive groups can also be cross-linked by photoexposure. However, during thermal imidisation process, both cross-linked and non-cross-linked photosensitive groups are debonded by the imide-ring closure formation, regardless of the photoexposure, and ultimately outgassed[9–11]. In addition, the photopackage components added are always designed to be outgassed by the conventional thermal baking process. In fact, outgassing of the photoactive groups and the

photopackage components depends strongly upon the bake condition as well as their boiling points and degradation temperatures. If they are not completely removed by the thermal imidisation process and then remained as residues at a certain level, the residues would severely affect the structure and properties in the resultant polyimide film. Even though the photosensitive groups and the photo-package components are fully outgassed, they may influence the morphological structure of the precursor in the condensed state as well as the imidisation kinetics, consequently leading to the different structure and properties in the resultant polyimide.

According to a study reported recently by Ree et al.[9], the poly(p-phenylene biphenyltetracarboximide) film, which was prepared from its photosensitive precursor, exhibited a different structure and properties, in comparison to the corresponding polyimide film obtained from the poly(amic acid) precursor. That is, the molecular order and micro-structure in the PSPI film were observed to be enhanced. However, despite the enhancement in both the molecular order and microstructure, properties in the film plane, such as mechanical properties, thermal expansion, residual stress, optical properties and dielectric constant, degraded due to both the molecular in-plane orientation being disturbed and microvoids possibly generated by the bulky photosensitive group during the thermal imidisation.

Among properties in PSPI films, the water sorption characteristic is an interesting subject matter to be investigated with regard to the reliability and performance of electronic devices fabricated with PSPIs, because water causes metal corrosions, failures of the adhesion to metals, and degradation of dielectric properties[12-15]. For conventional polyimides (PIs), water sorption behaviours have been widely investigated using gas permeation analyser[16-19], electro-microbalance[16-26], quartz-spring microbalance[27-29], quartz-crystal microbalance[30], residual stress analyser[31-34], and capacitance tester[24]. In comparison to the conventional PIs, the water sorption behaviours in PSPIs have been rarely investigated. Recently, Ree et al.[9,31,32] have investigated water sorptions of several PSPIs with various chain rigidities in films adhered to silicon substrates rather than free-standing films through measurements of residual stress relaxation using a wafer bending technique. The results were then compared with those of the corresponding PIs prepared from the poly(amic acid) precursors. The studied polyimide back-bones were poly(p-phenylene pyromellitimide) (PMDA-PDA), poly(p-phenylene biphenyltetracarboximide) (BPDA-PDA), poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA), and poly(4,4'-oxydiphenylene benzo-phenonetetracarboximide) (BTDA-ODA). The stress relaxations in the films adhered to silicon substrates, due to water absorption, were measured at 25°C in 50% relative humidity (RH), and analysed by the Fickian process. The coefficients of water diffusion were estimated to be 1.4 × 10^{-10} to 42.1 × 10^{-10} cm²/s, depending on the polyimide backbone structures and precursor origins (namely, conventional and photosensitive precursors), as shown in *Table 1*. In particular, for the PMDA-PDA PSPI the coefficient of water diffusion could not be estimated because of its abnormal stress relaxation behaviour. Overall, the diffusion rates in the PSPIs were relatively fast in comparison to those of the corresponding conventional PIs. In this stress relaxation study, amounts of water absorbed in the films could not measured because of the inherent limitation of the wafer bending technique.

Table 1 Coefficients of water diffusion in thin films of PIs and PSPIs measured by residual stress relaxation technique[a]

| Films	Diffusion coefficient, D (× 10^{-10} cm²/s)	Film thickness (μm)
PMDA-PDA PI	9.2	9.2
PMDA-PDA PSPI	—	10.1
BPDA-PDA PI	1.4	12.4
BPDA-PDA PSPI	6.8	13.1
PMDA-ODA PI	16.5	12.8
PMDA-ODA PSPI	42.1	11.2
BTDA-ODA PI	7.1	12.4
BTDA-ODA PSPI	34.2	13.6

[a] Obtained from Refs [9,31,32]

In the present study, several PSPIs, including the PSPI systems described above, were examined in detail in free standing films rather than films adhered to substrates by gravimetry, with regard to water sorption and diffusion. The PSPI precursors were synthesised in N-methyl-2-pyrrolidone (NMP) by the acid/base complexations of the poly(amic acid) precursors with photochemically cross-linkable 2-(dimethylamino)ethyl methacrylate (*Figure 1*). The PSPI precursor solutions were cast and soft-baked. In order to investigate the effect of the photosensitive group itself to film properties, all the soft-baked precursor films were not exposed to u.v. light, and directly converted to the polyimide films through a conventional thermal imidisation process. For the PSPI films, water sorption and diffusion were measured at 25°C in 100% RH and compared with those of the corresponding PIs. The results were interpreted with the consideration of the solubility parameter, morphological structure, free-volume, voids, and residues.

EXPERIMENTAL

Materials and sample preparation

Poly(p-phenylene biphenyltetracarboxamic acid) (BPDA-PDA PAA) (ca. 40k $\bar{M}_w$; 13.5 wt% solid content) and poly(4,4'-oxydiphenylene pyromellitamic acid) (PMDA-ODA PAA) (ca. 35k $\bar{M}_w$; 16.0 wt%) precursor solutions were received from Du Pont Chemical Co. Poly(p-phenylene pyromellitamic acid) (PMDA-PDA PAA) (ca. 30k $\bar{M}_w$; 10.0 wt%), poly(4,4'-oxydiphenylene biphenyltetracarboxamic acid) (BPDA-ODA PAA) (ca. 40k $\bar{M}_w$; 18.0 wt%), and poly(4,4'-oxydiphenylene benzo-phenonetetracarboxamic acid) (BTDA-ODA PAA) (ca. 40k $\bar{M}_w$; 18.0 wt%) precursor solutions were prepared in NMP through polycondensation from the respective dianhydrides and diamines. Photosensitive precursor solutions were prepared by attaching photo-cross-linkable 2-(dimethylamino)ethyl methacrylate (DMAEM) to the orthoamic acid groups of the poly(amic acid)s through the acid/amine ionic complex formation as previously described elsewhere[9]: PMDA-PDA PSPI, PMDA-ODA PSPI, BPDA-PDA PSPI, BPDA-ODA PSPI, and BTDA-ODA PSPI precursors (*Figure 1* and *Figure 2*).

All the precursor solutions were spin-coated on glass slides and silicon substrates, followed by soft-baking on a hotplate at 80°C for 30 min. The soft-baked precursor films were thermally imidised in an oven with a dry nitrogen gas flow by an imidisation protocol: 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h with a ramping rate of
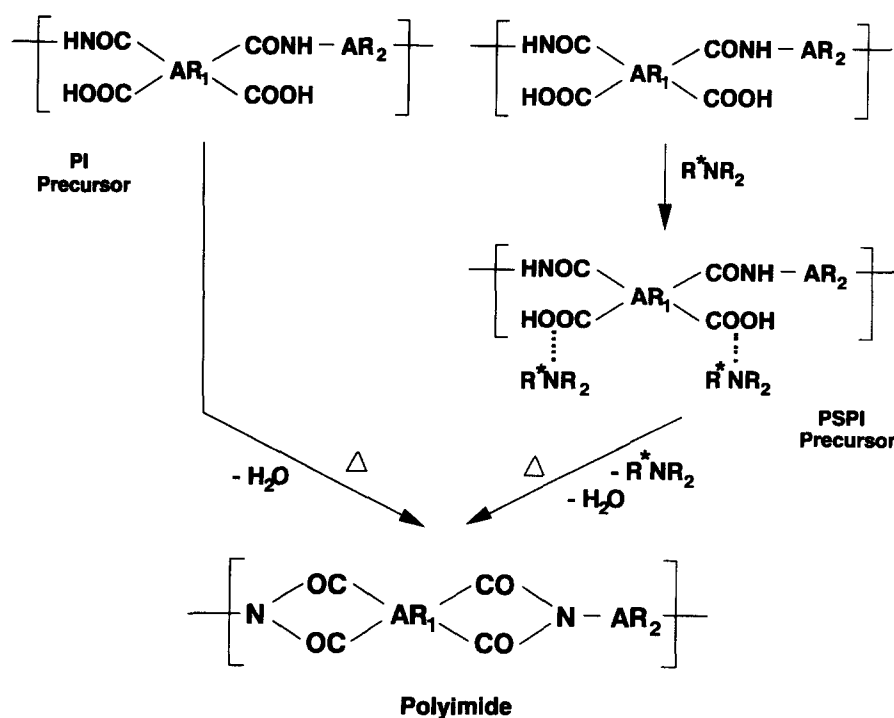
Figure 1 Polyimide formations from conventional polyimide (PI) precursors, poly(amic acid)s, as well as photosensitive polyimide (PSPI) precursors: AR_1 = phenyl, biphenyl, benzophenone; AR_2 = phenyl, 4,4'-oxydiphenyl; R* = photochemically cross-linkable ethyl methacrylate; NR_2 = dimethylamino

2.0 K/min. After the thermal imidisation, the samples were cooled at a rate of 1.0 K/min. Thicknesses of the imidised films were measured to be 9–16 μm, using an Alpha-stepper (Model 2000, Tencor Instruments). These films were taken off from the substrates with the aid of either deionised (DI) water or very diluted hydrofluoric acid solution and washed with DI water several times, followed by drying for 2 days at 100°C in a vacuum of 5 × 10⁻⁴ torr. For measurements of

Figure 2 Chemical structures of polyimides prepared from conventional and photosensitive precursors

water sorption, films were cut to a size of 12 × 15 mm using blades.

Measurements

For PSPI and PI films, water diffusion and uptake were measured in 100% RH at 25°C as a function of time, using an electromicrobalance (Cahn Instruments, Model 2000) with a resolution of 1 μg over ≤ 20 mg weight loading as described previously in the literature[20–22]. A film specimen was hung from a platinum wire of the balance arm in the sample chamber. The sample chamber was purged with dried nitrogen, and the specimen was dried further in a high vacuum of 2 × 10⁻⁶ torr for 2–3 days. Then, the sample chamber with the dried film specimen was again purged very slowly with dried nitrogen, finally reaching atmospheric pressure. Under slow purging of dried nitrogen, distilled water was carefully introduced into the chamber until the water level was close to the film specimen by a gap of 5–10 mm, resulting in 100% RH in the chamber. The nitrogen purging was stopped immediately after the completion of water filling. Here, the water filling was completed within *ca.* 15 s. Then, the water sorption in the film specimen was monitored as a function of time. After completion of the measurement, water was drained out from the chamber, and the film specimen was again dried for 3 days under vacuum. Then, the water sorption in the film was again measured after the sample chamber was refilled with water in the same way as aforementioned. This water sorption measurement was repeated three to five times for each sample.

The refractive indices of the films were measured using a prism coupler (Metricon Company Model 2010) or a similar prism coupler made in our laboratory, which was equipped with a He–Ne laser light source of 632.8 nm wavelength and controlled by a personal computer. The refractive index was measured in transverse electric (TE: $n_{TE} = n_{xy}$, refractive index in the film plane) and transverse magnetic (TM: $n_{TM} = n_z$, refractive index in the direction of film
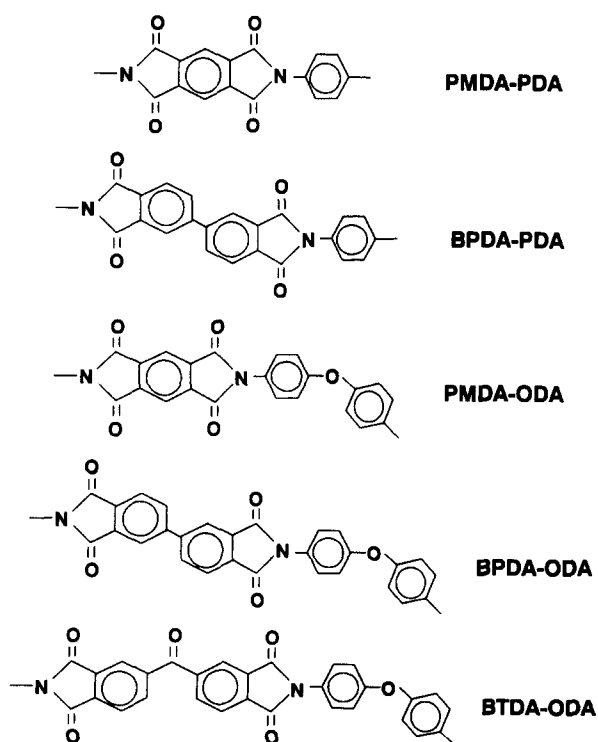
thickness) modes by choosing the appropriate polarisation of the incident laser beam as described elsewhere[9,20,21,35,36]. All measurements were performed using a cubic zirconia prism of $n_{TE} = n_{TM} = 2.1677$ at 632.8 nm. The birefringence ($\Delta = n_{xy} - n_z$), which is a measure of the molecular orientation in the film, was estimated from the refractive indices.

For dynamic mechanical tests, some of the imidised films were diced into strips of 6.350 mm width using circular blades before removal from the substrates. Dynamic mechanical thermal properties were measured in nitrogen ambient over the range of 25–500°C, using a tensile head based dynamic mechanical thermal analyser (DMTA) (Polymer Laboratories Model Mark-II) controlled by a personal computer. The employed heating rate and frequency were 10.0 K/min and 10 Hz, respectively. The grip gauge length was 5.0 mm.
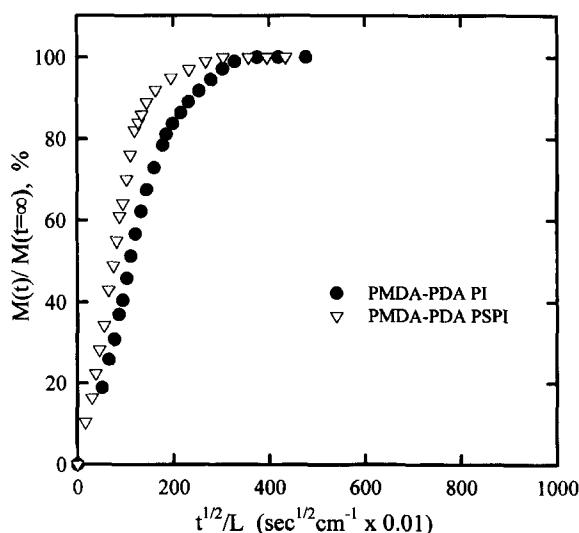
RESULTS AND DISCUSSION

Water sorption and diffusion behaviour

Water sorption isotherms of PIs and PSPIs in thin films, which were measured at 25°C in 100% RH, apparently followed the Fickian process well. In addition, PMDA-ODA and BPDA-PDA polyimides in films of 10–110 μm thick have previously been reported to nearly exhibit Fickian water sorption behaviours over 22–100% RH despite the morphological heterogeneities due to the ordered and disordered phases[20-22]. Thus, all sorption isotherms measured in the present study were analysed with the following equation, which is the mathematical solution for the water diffusion in an infinite slab with a constant surface concentration[37]:

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

(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.

The measured water sorption isotherms are shown in *Figure 3*, *Figure 4*, *Figure 5*, *Figure 6* and *Figure 7*, and the analysed results are summarised in *Table 2*. *Figure 3* shows water sorption isotherms of PMDA-PDA PI and PSPI in thin films. From the best fittings of the isotherms by equation (1), the coefficient of water diffusion was estimated to be 3.7 × 10^{-10} cm²/s for the PMDA-PDA PI and 9.5 × 10^{-10} cm²/s for the PMDA-PDA PSPI. The water uptake in equilibrium was 5.7 wt% for the PI and 5.9 wt% for the PSPI. The results indicate that water was diffused more quickly into the PSPI than the PI, but amounts of water absorbed in the films were very close to each other.

The BPDA-PDA PI film exhibited 1.4 × 10^{-10} cm²/s coefficient of water diffusion and 1.3 wt% water uptake. The corresponding PSPI film revealed 5.0 × 10^{-10} cm²/s
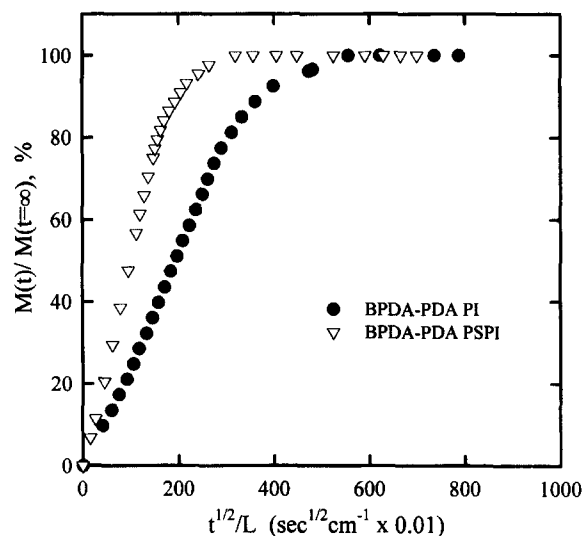
Figure 4 Isotherms of water sorption in films of BPDA-PDA PI and PSPI measured at 25°C in 100% RH. The PI and PSPI films were prepared from the poly(amic acid) and the photosensitive precursors by thermal imidisation at 400°C, respectively. The thickness of the films was 12.4–13.1 μm

Figure 3 Isotherms of water sorption in films of PMDA-PDA PI and PSPI measured at 25°C in 100% RH. The PI and PSPI films were prepared from the poly(amic acid) and the photosensitive precursors by thermal imidisation at 400°C, respectively. The thickness of the films was 9.2–10.1 μm
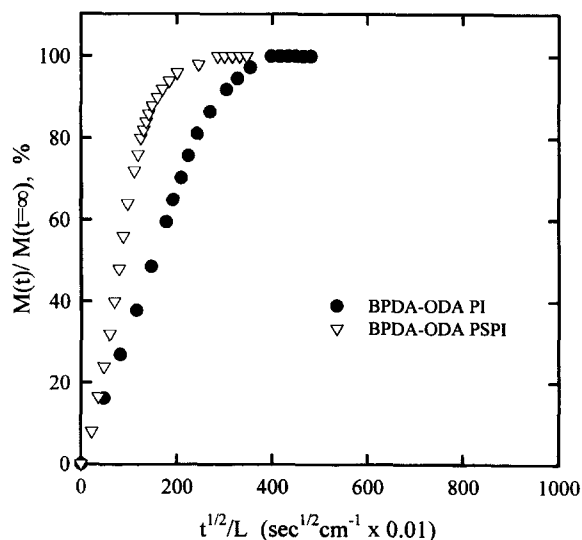
Figure 5 Isotherms of water sorption in films of BPDA-ODA PI and PSPI measured at 25°C in 100% RH. The PI and PSPI films were prepared from the poly(amic acid) and the photosensitive precursors by thermal imidisation at 400°C, respectively. The thickness of the films was 13.1–15.5 μm
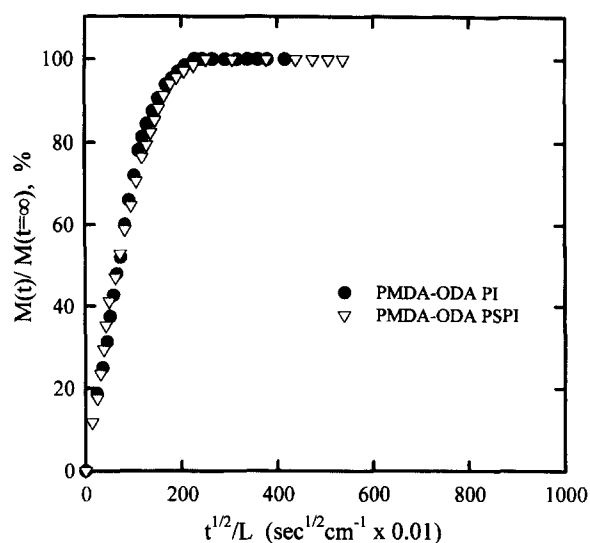
Figure 6 Isotherms of water sorption in films of PMDA-ODA PI and PSPI measured at 25°C in 100% RH. The PI and PSPI films were prepared from the poly(amic acid) and the photosensitive precursors by thermal imidisation at 400°C, respectively. The thickness of the films was 11.2–12.8 μm
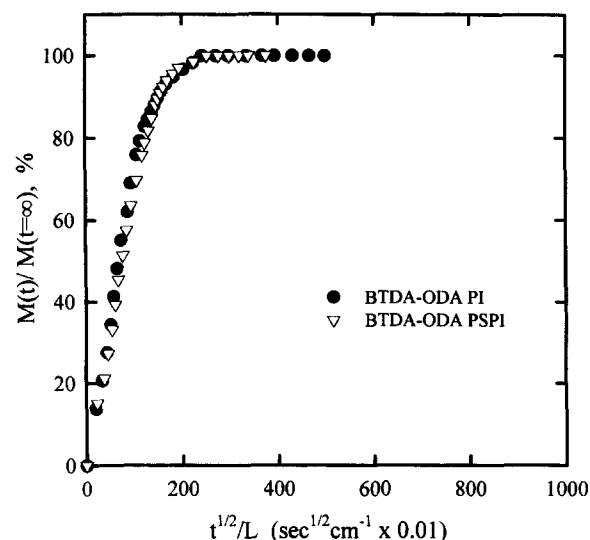

Figure 7 Isotherms of water sorption in films of BTDA-ODA PI and PSPI measured at 25°C in 100% RH. The PI and PSPI films were prepared from the poly(amic acid) and the photosensitive precursors by thermal imidisation at 400°C, respectively. The thickness of the films was 12.4–13.6 μm

Table 2 Coefficients of water diffusion and water uptakes in thin films of PIs and PSPIs measured by gravimetry

| Films	Diffusion Coefficient, D ($\times 10^{-10}$ cm^2/s)	Water uptake $M(\infty)$, (wt%)	Film thickness (μm)
PMDA-PDA PI	3.7	5.7	9.2
PMDA-PDA PSPI	9.5	5.9	10.1
BPDA-PDA PI	1.4	1.3	12.4
BPDA-PDA PSPI	5.0	1.8	13.1
BPDA-ODA PI	3.0	1.4	13.1
BPDA-ODA PSPI	8.3	1.5	15.5
PMDA-ODA PI	10.5	2.5	12.8
PMDA-ODA PSPI	8.7	2.6	11.2
BTDA-ODA PI	10.0	2.2	12.4
BTDA-ODA PSPI	9.0	2.6	13.6

coefficient of water diffusion and 1.8 wt% water uptake. In this case, the PSPI film showed a higher diffusion coefficient and a higher uptake of water than the PI film (*Figure 4*).

Similar behaviour was observed in BPDA-ODA films, as shown in *Figure 5*. The BPDA-ODA PSPI film showed a relatively high coefficient of water diffusion, 8.3 $\times$ 10^{-10} cm^2/s, compared to that of the corresponding PI film (3.0 $\times$ 10^{-10} cm^2/s). However, the amount of water absorbed in the PSPI film was very similar to that of the PI film.

However, water sorption behaviours in both PMDA-ODA and BTDA-ODA polyimides are somewhat different from the polyimides aforementioned. As shown in *Figure 6* and *Figure 7*, the PSPIs apparently revealed water sorption isotherms similar to those of the corresponding PIs, respectively. For PMDA-ODA polyimide, the PSPI film exhibited 8.7 $\times$ 10^{-10} cm^2/s coefficient of water diffusion and 2.6 wt% water uptake, whereas the PI film revealed 10.5 $\times$ 10^{-10} cm^2/s coefficient of water diffusion and 2.5 wt% water uptake. The PSPI film showed a relatively lower diffusion coefficient of water than the PI. However, the levels of water absorbed in the films were almost the same. In the case of BTDA-ODA polyimide, the PSPI film revealed a relatively low coefficient of water diffusion, however, the water uptake was relatively high in comparison with the PI film.

Here, it is worth comparing the results of the present study to the results reported previously. As mentioned earlier in the introduction section, some of the polyimides were previously investigated by residual stress relaxation at 50% RH, rather than 100% RH[9,31,32]. In the measurements, only coefficients of water diffusion were estimated. The results are illustrated in *Table 1*. In comparison, both the stress relaxation technique and the gravimetry gave the same coefficients of water diffusion for the BPDA-PDA PI film in spite of different humidity conditions in the measurements (*Table 1* and *Table 2*). However, a discrepancy in the measurements of both techniques was observed even for the BPDA-PDA PSPI film. That is, the coefficient of water diffusion measured by the stress relaxation analysis was 36% as high as that measured by the gravimetry. The discrepancy between the measurements of both techniques was further significant for the other PIs and PSPIs. For example, the coefficients of water diffusion in the PMDA-ODA PSPI and the BTDA-ODA PSPI were approximately three times higher than those measured by the gravimetry, respectively. The discrepancies are not fully understood. However, the discrepancies could arise for several reasons: first, films adhered to silicon substrates were employed in the stress relaxation analysis, whereas free-standing films were used in the gravimetry; second, the residual stress generated at the interfaces of films and silicon substrates might cause the acceleration of water diffusion into the film as well as the interface, leading to the relatively high water diffusion; and third, the two techniques have different sensitivities in the measurement.

For comparison, the isotherms of water sorption for all the PIs are plotted together in *Figure 8*, whereas those for all the PSPIs are shown in *Figure 9*. For the PIs, water sorption behaviours are quite different from each other, strongly depending upon the sort of polyimide. The coefficient of water diffusion varies in the range of 1.4 $\times$ 10^{-10} cm^2/s to 10.5 $\times$ 10^{-10} cm^2/s, and is in the increasing order: BPDA-PDA PI < BPDA-ODA PI < PMDA-PDA PI < BTDA-ODA PI < PMDA-ODA PI. The water uptake varies from
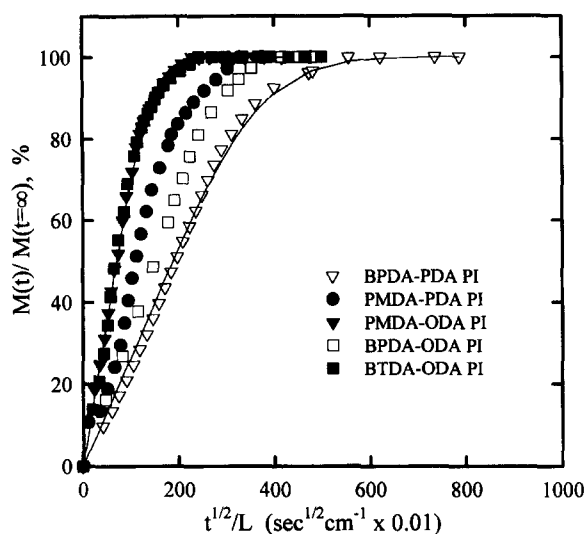
Figure 8 Isotherms of water sorption in films of various PIs measured at 25°C in 100% RH. All the PI films were prepared from their poly(amic acid)s by thermal imidisation at 400°C. The thickness of the films was 9.2–13.1 μm
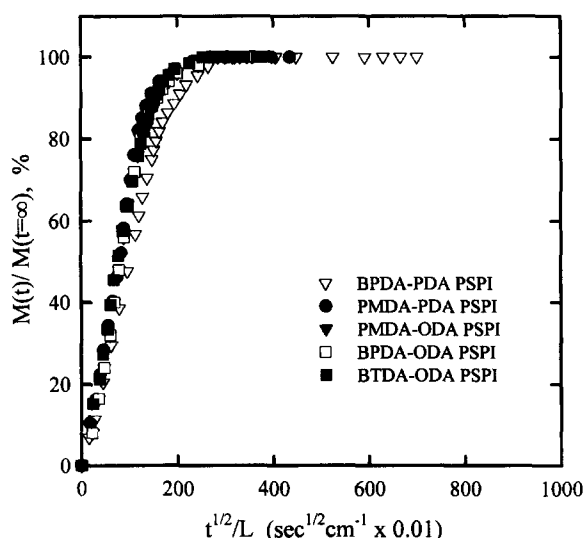
Figure 9 Isotherms of water sorption in films of various PSPIs measured at 25°C in 100% RH. All the PSPI films were prepared from their photosensitive precursors by thermal imidisation at 400°C. The thickness of the films was 10.1–15.5 μm

1.3 to 5.7 wt%, and is in the increasing order: BPDA-PDA PI < BPDA-ODA PI < BTDA-ODA PI < PMDA-ODA PI < PMDA-PDA PI.

The large difference in the water sorptions of the PIs is not preserved for the corresponding PSPIs (*Figure 9*). In particular, the large difference in the coefficients of water diffusion of the PIs was significantly reduced in the PSPIs: coefficients of water diffusion in the PSPIs are in the range of 5.0 × 10⁻¹⁰ cm²/s to 9.5 × 10⁻¹⁰ cm²/s. For PMDA-PDA, BPDA-PDA, and BPDA-ODA, the diffusion coefficients increased significantly in the PSPI films. In contrast, for PMDA-ODA and BTDA-ODA, the PSPI films exhibited slightly lower diffusion coefficients than the corresponding PI films, respectively. However, all the PSPI films, except for the BPDA-PDA PSPI film, revealed water uptakes similar to those of the corresponding PI films: the water uptakes are in the range of 1.5–5.9 wt%. In particular, the water uptake in the BPDA-PDA PSPI was significantly

increased, in comparison to that of the corresponding PI. Consequently, the coefficient of water diffusion is in the increasing order: BPDA-PDA PSPI < BPDA-ODA PSPI < PMDA-ODA PSPI < BTDA-ODA PSPI < PMDA-PDA PSPI, whereas the water uptake is in the increasing order: BPDA-ODA PSPI < BPDA-PDA PSPI < PMDA-ODA PSPI~BTDA-ODA PSPI < PMDA-PDA PSPI.

These water sorption behaviours in the PIs and PSPIs can be interpreted by considering two major contributory factors, morphological structure and chemical affinity to water. Regarding chemical backbones, the chemical affinity of dianhydride monomeric units to water is in the increasing order: BPDA < PMDA < BTDA, whereas for diamine units it is in the increasing order: PDA < ODA[30,38]. In addition, for some of the PIs in films, surface energies were recently measured by contact angle measurements with the aid of a series of organic solvents with known surface energies: 32 dyne/cm for BPDA-PDA PI and 41 dyne/cm for PMDA-ODA PI[22]. Water has a surface energy of 73 dyne/cm, therefore, BPDA-PDA is more hydrophobic than PMDA-ODA. From both the chemical affinities and the surface energies, one can simply expect that the water sorption in the film is in the increasing order: BPDA-PDA PI < BPDA-ODA < PMDA-PDA < PMDA-ODA < BTDA-ODA. This prediction is in good agreement with the water diffusion coefficients in the PIs. However, the water uptakes in the PIs do not follow the prediction. In particular, the PMDA-PDA showed the highest water uptake in spite of its relatively low chemical affinity to water.

The deviation from the prediction is significant in the PSPIs. The PMDA-PDA PSPI film exhibited both a higher diffusion coefficient and water uptake than PMDA-ODA PSPI and BTDA-ODA PSPI. The BPDA-PDA PSPI also revealed higher water uptake than BPDA-ODA PSPI. In addition, for PMDA-PDA, BPDA-PDA, and BPDA-ODA, the PSPI films quickly absorbed more water than the corresponding PI films, respectively. On the other hand, PMDA-ODA and BTDA-ODA PSPI films exhibited slightly lower diffusion coefficients and higher water uptakes than the corresponding PI films, respectively. From these results, it is suggested that in addition to the chemical affinity to water, the morphological structure term, which includes molecular order, chain orientation, free-volume, viods, and residues, may play an important role in the water sorption.

Morphological structure and glass transition behaviour

PMDA-PDA PI in films was previously reported to reveal only multiple diffraction peaks from the high chain ordering along the chain axis, in addition to the amorphous halo peak in the transmission wide-angle X-ray diffraction (WAXD) patterns, but exhibit only the amorphous halo peak in the reflection pattern[39,40]. These indicate two structural pieces of information. First, the polymer chains are mainly oriented in the film plane. Second, the polymer chains are highly ordered due to the rodlike chain nature, but irregularly packed together. The lack of regular intermolecular packing might be the result of the limited chain mobility due to its high glass transition temperature (T_g) during the thermal imidisation of the precursor. In fact, PMDA-PDA does not show any glass transition over the range of process temperatures: its T_g may be much higher than the decomposition temperature. Overall, the reflection and transmission WAXD patterns in the PI film were identical to those of the PSPI film, respectively. Mean intermolcular distances were estimated from the peak maximum of

amorphous halos; the results are presented in *Table 3*. The intermolecular distance in the film plane, which was estimated from the transmission pattern, was 4.97 Å for both the PI and PSPI films, however, that in the out-of-plane was 4.26 Å for the PI and 4.28 Å for the PSPI. That is, both the PI and PSPI films revealed almost the same intermolecular distances. However, for both the PI and PSPI films, the intermolecular distance was relatively higher in the transmission patterns than in the reflection patterns. Consequently, the results indicate that the rodlike polyimide chains were favourably oriented in the film plane so that they were more densely packed in the direction of film thickness than in the film plane.

The in-plane orientation of the polymer chains was also detected in the refractive index measurements, as shown in *Table 4*. The out-of-plane birefringence, which is a measure of polymer chain orientation, was calculated from the measured refractive indices to be relatively very high: 0.2300 in the PI film and 0.2303 in the PSPI. That is, the degrees of in-plane chain orientation in the PI and PSPI films are almost the same. Consequently, the molecular order and chain orientation in the PMDA-PDA polyimide

Table 3 Mean intermolecular distances in thin films of PIs and PSPIs[a]

Thin films	Mean intermolecular distances[b]		
	In-plane[c] (Å)	Out-of-plane[d] (Å)	Film thickness (μm)
PMDA-PDA PI	4.97	4.26	9.2
PMDA-PDA PSPI	4.97	4.28	10.1
BPDA-PDA PI	4.94	4.89	12.4
BPDA-PDA PSPI	4.94	4.89	13.1
BPDA-ODA PI	4.90	4.90	13.1
BPDA-ODA PSPI	4.90	4.90	15.5
PMDA-ODA PI	4.94	4.89	12.8
PMDA-ODA PSPI	4.84	4.80	11.2
BTDA-ODA PI	4.89	5.37	12.4
BTDA-ODA PSPI	4.91	5.39	13.6

[a]Obtained from Refs [10,39–41] [b]Estimated from the maxima of X-ray diffraction peaks corresponding to the intermolecular spacing [c]Calculated from the peak maximum of amorphous halos in the transmission WAXD patterns [d]Calculated from the peak maximum of amorphous halos in the reflection WAXD patterns

Table 4 Refractive indices and out-of-plane birefringences of PIs and PSPIs in thin films

Thin films	Optical properties at 632.8 nm			
	In-plane refractive index (n_{xy})	Out-of-plane refractive index (n_z)	Out-of-plane birefringence (Δ)	Film thickness (μm)
PMDA-PDA PI	1.8164	1.5864	0.2300	9.2
PMDA-PDA PSPI	1.8186	1.5883	0.2303	10.1
BPDA-PDA PI	1.8549	1.6129	0.2420	12.4
BPDA-PDA PSPI	1.8266	1.6263	0.2003	13.1
BPDA-ODA PI	1.7536	1.6919	0.0617	13.1
BPDA-ODA PSPI	1.7534	1.6921	0.0613	15.5
PMDA-ODA PI	1.7279	1.6424	0.0855	12.8
PMDA-ODA PSPI	1.7277	1.6426	0.0851	11.2
BTDA-ODA PI	1.6903	1.6737	0.0166	12.4
BTDA-ODA PSPI	1.6905	1.6741	0.0164	13.6

apparently were not influenced by the bulky photosensitive groups.

However, the effect of the photosensitive group was pronounced in the BPDA-PDA PSPI[10]. BPDA-PDA is known to form a crystal structure based on the orthorhombic unit cell with a space group of $Pba2$[39,41]. The transmission WAXD patterns showed mainly (00*l*) peaks, such as (004), (0010), (0014) and (0016), in addition to the (110) peak. These multiple (00*l*) peaks have appeared only in the transmission patterns, indicating that the polyimide molecules ordered highly along the chain axis are preferentially aligned in the film plane. The (004) peak was apparently not influenced in shape by the photosensitive group. However, the higher ordered (0010), (0014) and (0016) became weak and broad in the PSPI film. These indicate that the high in-plane chain orientation was degraded somewhat in the PSPI film. This was evident in the refractive index measurements. As shown in *Table 4*, the birefringence was decreased to 0.2003 in the PSPI film from 0.2420 in the PI film. The reflection pattern, which exhibits only (110), (200) and (210) peaks, was also influenced by the photosensitive group. The intensity of the (110) peak drastically increased in the PSPI film. The (210) peak was little changed, while the (200) peak was significantly weakened in intensity but became narrower in width. The crystallinity also increased to 24% in the PSPI film from 18% in the PI film. However, the mean intermolecular distances in both the PI and PSPI films were the same: 4.94 Å in the film plane and 4.89 Å in the out-of-plane (*Table 3*).

BPDA-ODA revealed crystalline like diffraction patterns with a big amorphous halo[40]. The transmission pattern is almost identical with the reflection pattern in both the PI and PSPI films. They showed approximately eight diffraction peaks seated on the big amorphous halo peak over the angle range of 10 to 30° (2θ) in the diffraction patterns obtained with the aid of CuK$_\alpha$ radiation source: here, 2θ is the diffraction angle. From the diffraction patterns, it is expected that BPDA-ODA forms a crystal structure similar to that observed for the BPDA-PDA, although its overall crystallinity is much less than that of the BPDA-PDA. However, the structure of BPDA-ODA is not fully characterised yet. Mean intermolecular distances were roughly estimated from the diffraction patterns because the amorphous halos were very big and broad: 4.9 Å in the film plane as well as the out-of-plane, regardless of the PI and PSPI. For the PI and PSPI films, birefringences were relatively small: 0.0617 for the PI and 0.0613 for the PSPI. That is, the degree of in-plane chain orientation was very small in the BPDA-ODA. Conclusively, the chain order and orientation in the BPDA-ODA was not changed sensitively by the photosensitive group.

A similar effect of photosensitive group was observed in the structure of PMDA-ODA[10]. Regardless of the precursor origin, PMDA-ODA exhibited a sharp diffraction peak at the low angle region, which corresponds to the chain order along the chain axis, and a big amorphous halo peak in the the transmission pattern, but only the big amorphous halo peak in the reflection pattern. This indicates that PMDA-ODA showed a reasonably high chain ordering along the chain axis, but was irregularly packed as observed in the rodlike PMDA-PDA. PMDA-ODA molecules were also oriented favourably in the film plane despite the bend chain conformation. The in-plane chain orientation was also evident in the birefringence: the birefringence was 0.0855 for the PI and 0.0851 for the PSPI. For the PSPI film, the diffraction peaks were enhanced in intensity. In addition, the

mean intermolecular distances were slightly decreased in the PSPI film: for the PI, 4.94 Å in the film plane and 4.89 Å in the out-of-plane, whereas for the PSPI, 4.84 Å in the film plane and 4.80 Å in the out-of-plane. Conclusively, PMDA-ODA chains were relatively more ordered in the PSPI film than the PI film.

In contrast to the polyimides described above, BTDA-ODA PI and PSPI exhibited only featureless amorphous halo in both reflection and transmission patterns[10]. The diffraction patterns of the PSPI were identical to those of the PI. Therefore, only mean intermolecular distances were estimated from the amorphous halos: for the PI, 4.89 Å in the film plane and 5.37 Å in the out-of-plane, whereas for the PSPI, 4.91 Å in the film plane and 5.39 Å in the out-of-plane. The intermolecular distance was shorter in the film plane than the direction of film thickness. However, the films were still weakly anisotropic in the chain orientation, leading to the weak birefringence of 0.0164 to 0.0166.

As described above, the molecular ordering was enhanced by the photosensitive group in both BPDA-PDA and PMDA-ODA, but varied little on the other polyimides. In addition, for BPDA-PDA the molecular in-plane orientation was significantly degraded by the photosensitive group, whereas for the other polymers it was influenced very little. In general, for a given polymer water diffusion is relatively slower in the crystalline phase than the amorphous phase. Thus, it is expected that the molecular orders enhanced in the PSPI films restrict water diffusion, leading to the low coefficient of water diffusion and water uptake. The coefficients of water diffusion for PMDA-ODA are in good agreement with the prediction. However, the water uptake did follow the expectation: that is, the PSPI film absorbed more water than the PI film. For BPDA-PDA, the result was totally contradicted the expections: the PSPI film revealed higher water diffusion and water uptake than the PI film. Furthermore, both PMDA-PDA and BPDA-ODA PSPI exhibited significantly higher coefficients of water diffusion and slightly higher water uptakes than the corresponding PIs, respectively, although their molecular orders were not influnced by the photosensitive group. In contrast, the BTDA-ODA PSPI showed a slightly lower coefficient of water diffusion and slightly higher water uptake than the PI, in spite of no difference between the molecular orders. From these results it is suggested that the variations in the molecular order and orientation, which were caused by the photosensitive group, are not the major factors to water sorption behaviours in the PSPIs.

In addition to the molecular order and orientation, voids, which are possibly formed in the PSPI films, should be considered as a clue to influencing the water sorption behaviours. During the thermal imidisation, the bulky photosensitive groups in the soft-baked film debond from the polymer backbone and then outgas through evaporation as well as thermal degradation. Through this outgassing process, voids may be generated in the resulting film and, at the same time, they may be healed in a certain degree by volume shrinkage. However, the healing of the voids is really dependent upon the chain mobility during the imidisation. The chain mobility is directly related to the T_g, which is a measure of chain flexibility. The higher chain flexibilty leads to the lower T_g, providing the higher chain mobility. Thus, voids may be healed more easily in the low T_g polyimide than the high T_g polymer.

T_g's of the PIs and PSPIs were examined by DMTA. The dynamic storage moduli measured with varying temperature are shown in *Figure 10*. Here, for each polyimide, the
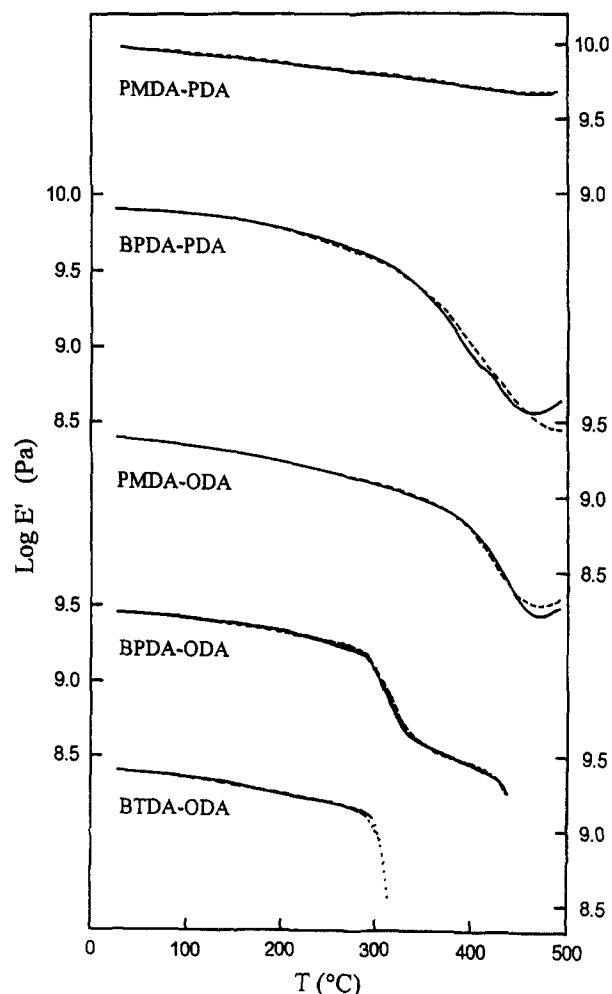
Figure 10 Variations of dynamic storage moduli (E's) with temperature in various PIs and PSPIs in thin films. Here, for a given polyimide the storage modulus profiles of the PI and PSPI films were superimposed in order to compare them both: (———), PI; (- - -), PSPI. Measurements were performed with a heating rate of 10.0 K/min at a frequency of 10 Hz under dried nitrogen atmosphere. The thickness of all the films was 9.2–15.5 μm.

storage modulus profile of the PI film was superimposed with that of the PSPI film in order to compare them both. For all the polyimides, their storage modulus profiles were apparently not affected in shape by the photosensitive group. That is, for a gievn polyimide, the T_g in the PSPI film was the same as that of the PI film. From the storage modulus profiles, T_g, the onset temperature of glass transition, was estimated to be 320°C for BPDA-PDA, 385°C for PMDA-ODA, 289°C for BPDA-ODA, and 285°C for BTDA-ODA. PMDA-PDA did not show any glass transition over 25–500°C, indicating that its T_g is higher than 500°C.

In the case of PMDA-PDA, when its precursors are converted to the polyimides during the thermal imidisation, the imidised polymer chains are immediately frozen because the T_g is higher than the imidisation temperature. Under this circumstance, voids generated by the bulky photosensitive groups may not be healed completely during the imidisation process. The unhealed voids may positively contribute to the water sorption, resulting in the relatively high water sorption in the PSPI film. Even though PMDA-PDA PI has a low chemical affinity to water, it exhibits a relatively high water sorption. This might result from the coarse molecular packing which was induced by the frozen polymer chains because the T_g is higher than the imidisation

temperature. This is evident in the large difference between the mean intermolecular distances in the film plane and in the out-of-plane (*Table 3*). That is, a high degree of free volume was generated in the film plane.

In comparison to PMDA-PDA, BPDA-PDA is relatively less rigid. Its T_g is lower than that of PMDA-ODA. However, above T_g its storage modulus is always higher than that of PMDA-ODA, indicating that BPDA-PDA is less mobile than PMDA-ODA. The limited chain mobility in BPDA-PDA may restrict the healing of voids generated by the photosensitive groups. Thus, the partially unhealed voids may cause an increase in the water sorption. However, both PMDA-ODA and BTDA-ODA are relatively much more flexible than PMDA-PDA and BPDA-PDA. Thus, for both PMDA-ODA and BTDA-ODA PSPIs, voids generated by the photosensitive groups might be healed completely.

For BPDA-ODA, its T_g is lower than that of PMDA-ODA, but very close to that of BTDA-ODA, indicating that its chain mobility is between those of PMDA-ODA and BTDA-ODA. However, its water sorption behaviour was highly affected by the photosensitive groups. This may related to the residues in the PSPI film, which were perhaps generated by the photosensitive groups. BPDA-ODA PI exhibited a relatively low coefficient of water diffusion as well as a quite low water uptake, indicating that it has an inherently low permeability. The low permeability may play a role in trapping the debonded photosensitive groups and their degraded products in part in the PSPI film during the thermal imidisation, resulting in the residues in the film. The residues may postively contribute to the water sorption, consequently leading to the relatively high water sorption. In addition, BPDA-PDA PI exhibits a lower coefficient of water diffusion and lower water uptake than BPDA-ODA, so that the tendency to trap residues in films could be higher in the BPDA-PDA PSPI than the BPDA-ODA PSPI. Thus, the relatively pronounced water sorption in the BPDA-PDA PSPI might be partially attributed to the residues trapped in the film.

CONCLUSIONS

Several PSPI precursors were synthesised by the acid/base complexations of conventional poly(amic acid) precursors with photochemically crosslinkable 2-(dimethyl-amino)ethyl methacrylate. PSPIs in films were prepared from the photosensitive precursors by thermal imidisation, whereas the corresponding PIs in films were prepared from the conventional poly(amic acid)s. Water sorption and diffusion behaviours in the PSPIs were gravimetrically measured at 25°C in 100% RH and compared with those of the corresponding PIs. For the PSPIs as well as the PIs, the water sorption and diffusion behaviours were nearly Fickian, regardless of the backbone chemistry. However, both coefficient of water diffusion and water uptake in the polyimide film were strongly dependent upon the backbone chemistry and precursor origin. For one group of poly-imides, including PMDA-PDA, BPDA-PDA and BPDA-ODA, the PSPIs absorbed water more quickly than the corresponding PIs, whereas for the other group of polyimides, including PMDA-ODA and BTDA-ODA, the PSPIs absorbed water less quickly than the corresponding PIs. In contrast to the water diffusion, for all the polyimides except BPDA-PDA, the water uptake was slightly higher in the PSPI film than the corresponding PI. For BPDA-PDA, the water uptake was much higher in the PSPI film than the PI film.

Overall, the bulky photosensitive groups affected the water diffusion and sorption behaviours in all the resultant polyimides negatively or positively, although they were debonded from the backbones and ultimately outgassed during the thermal imidisation process. All the measured water sorption and diffusion behaviours in the PSPIs were understood taken into the consideration of changes in the morphological structure (namely, chain order and orientation), voids, and residues possibly induced by the bulky photosensitive groups, in addition to the T_g's as well as the chemical affinities of the polyimide backbones to water.

The present study was restricted to PSPIs in thin films which were prepared from only the precursors unexposed to u.v. light. However, in the microelectronics industry, a PSPI precursor is processed either alone or through formulation with a photopackage using a conventional lithographic process with the aid of u.v. light sources. When a PSPI precursor in soft-baked films is exposed to u.v. light sources, its photosenstive groups are photochemically reacted together partially or fully, depending on the exposure energy and quantum efficiency. The photo-cross-linking reaction occurs intermolecularly as well as intra-molecularly, severely disturbing the morphological structure in the soft-baked precursor film. The disturbed morphological structure may be reflected on the molecular order and orientation in the resultant polyimide film. In addition, the photosensitive groups become very bulky due to the photo-cross-linking reaction, so that they can not be easily evaporated from the film during thermal imidisation even though debonded from the polymer backbone by the imide-ring closure formation. The cross-linked photo-sensitive groups, which are debonded from the polymer backbone by imidisation, may be degassed out from the film by only thermal decomposition. Thus, polyimide films, which are prepared from the soft-baked PSPI precursors exposed to u.v. light, may have more defects and residues, compared to those prepared without any u.v. light exposure. However, amounts of defects and residues are dependent upon the thermal imidisation condition: higher imidisation temperature and longer baking time may reduce levels of defects and residues. Conclusively, the effect of photo-sensitive groups on properties may be pronounced in the polyimide films obtained from the soft-baked PSPI precursors exposed to u.v. light. The effect of UV light exposure in the properties of PSPIs is currently conducted in our laboratory, and the results will be reported in a following paper.

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