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Effects of precursor origins on water sorption behaviors of various aromatic polyimides in thin films

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Abstract

Poly(amic diethyl ester) [PAE] precursors of four different polyimides with various chain rigidities were synthesized and thermally converted to the polyimides in thin films: rodlike poly(*p*-phenylene pyromellitimide) [PMDA-PDA] and poly(4,4′-biphenylene pyromellitimide) [PMDA-BZ], pseudo-rodlike poly(*p*-phenylene biphenylenetetracarboximide) [BPDA-PDA] and semiflexible poly(4,4-oxydiphenylene pyromellitimide) [PMDA-ODA PAE]. For the polyimide films, water sorption behaviors were investigated by gravimetry and then compared with those of the polyimides prepared from the corresponding poly(amic acid) [PAA] precursors. In addition, their morphological structures were examined by X-ray diffraction. For all the polyimides, both water sorption and morphological structure were dependent upon the history of precursor origin. All the polyimides except PMDA-ODA revealed relatively higher diffusion coefficient of water, higher water sorption, lower intermolecular packing order and lower population of a more ordered phase in the PAE-derived polyimide films than the corresponding PAA-derived polyimide films. For PMDA-ODA, the variations in the water diffusion and sorption due to the precursor origin were relatively small in spite of a relatively large change in the morphological structure. Overall, the effect of precursor origin on the water diffusion and sorption is significantly high in the rodlike or pseudo-rodlike polyimides having a high chain rigidity and high intermolecular packing order, but relatively low in the semiflexible polyimide with a relatively low chain rigidity. In comparison, regardless of the precursor origins, the diffusion coefficient of water was in the decreasing order PMDA-ODA $>$ PMDA-PDA $>$ PMDA-BZ $>$ BPDA-PDA and, however, the water sorption was in the decreasing order PMDA-PDA $>$ PMDA-BZ $>$ PMDA-ODA $>$ BPDA-PDA. These water diffusion and sorption behaviors were understood by considering their chemical affinities to water in addition to the morphological structures.

Keywords: Water sorption; Diffusion coefficient; Polyimides

1. Introduction

Aromatic polyimides are widely used in the microelectronic industry as interdielectric layers, passivation layers and alpha particle barriers because of their high thermal stability, relatively low dielectric constant, good mechanical properties, high chemical resistance and easy processability [1–3]. They are insoluble in most solvents so that they are processed in their soluble precursors and then imidized thermally or chemically [1–3]. One type of polyimide precursor is poly(amic acid) which is easily synthesized in an aprotic solvent from the polycondensation of dianhydride and diamine monomers [1,2]. However, poly(amic acid) is hydrolytically unstable since it is in equilibration with the constituent anhydride and amine [1,2,4]. Another type of polyimide precursor is poly(amic dialkyl ester) which is hydrolytically stable due to the absence of monomer–precursor equilibration [1,2,5,6]. Thus, in the microelectronic industry, poly(amic dialkyl ester) is considered as a polyimide precursor more adequate to the fabrication of devices, in spite of some inconvenience in the synthesis.

According to previous studies [6–9], poly(amic dialkyl ester) is known to show a thermal imidization behavior quite different from that of poly(amic acid). For example, poly(amic acid) of a polyimide is thermally imidized at a relatively low temperature, compared to its poly(amic dialkyl ester): the onset temperature of thermal imidization is ca. 130°C for poly(amic acid) and ca. 180°C for poly(amic dialkyl ester) [6–9]. The different imidization kinetics

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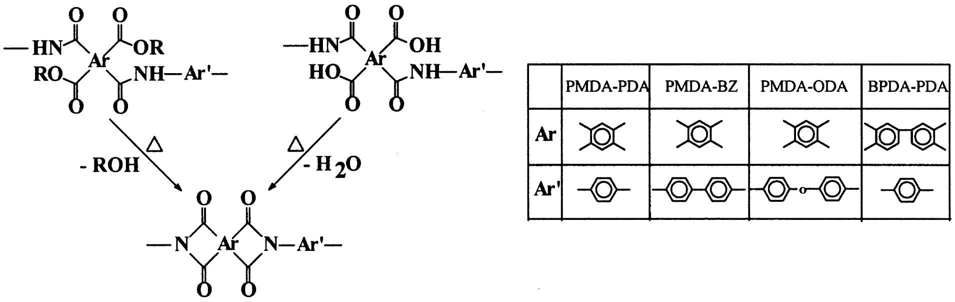

Fig. 1. Polyimides prepared from their poly(amic dialkyl ester) and poly(amic acid) precursors by thermal imidization: here, R is ethyl.

between the precursors of a polyimide may lead to different morphological structures and properties in the resultant polyimide, even though both the precursors provide the chemically identical polyimide. For the application of poly(amic dialkyl ester)s in the fabrication of devices, water sorption is one of the most important properties to be investigated, because the absorbed water is associated with degradation of dielectric properties and a variety of reliability problems, e.g. metal corrosion and interfacial delamination [10–12].

In the present study, poly(amic diethyl ester)s of four different polyimides with various chain rigidities, which are attractive to the industry, were synthesized and thermally converted to the polyimides in thin films (see Fig. 1). Water sorption behaviors were investigated in detail by gravimetry, and morphological structures were examined by X-ray diffraction. The measured water sorption characteristics were understood with considering the precursor origin and morphological structure in addition to the chemical affinity to water and, furthermore, compared to those of polyimides prepared from the corresponding poly(amic acid)s.

2. Experimental

Poly(*p*-phenylene pyromellitamic diethyl ester) [PMDA-PDA PAE] was synthesized by the low temperature polymerization of *p*-phenylene and pyromellitic diethyl ester diacyl chloride in dry *N*-methyl-2-pyrrolidone (NMP) as described elsewhere [5,6]. The other poly(amic diethyl ester)s were prepared in the same manner as PMDA-PDA PAE was synthesized: poly(4,4′-biphenylene pyromellitamic diethyl ester) [PMDA-BZ PAE], poly(4,4′-oxydiphenylene pyromellitamic diethyl ester) [PMDA-ODA PAE] and poly(*p*-phenylene biphenyltetracarboxamic diethyl ester) [BPDA-PDA PAE]. In addition, the corresponding poly(amic acid)s (PAAs) were synthesized in dry NMP from the respective dianhydrides and diamines, as reported previously in the literature [5,7,8]: poly(*p*-phenylene pyromellitamic acid) [PMDA-PDA PAA], poly(4,4′-biphenylene pyromellitamic acid) [PMDA-BZ PAA], poly(4,4-oxydiphenylene pyromellitamic acid) [PMDA-ODA PAA] and poly(*p*-phenylene biphenyltetracarboxamic acid) [BPDA-PDA PAA]. The intrinsic viscosity $[\eta]$ was measured at NMP at 30°C to be 0.474 dl/g for PMDA-PDA PAE, 0.520 dl/g for PMDA-BZ PAE, 0.503 dl/g for PMDA-ODA PAE, 0.850 dl/g for BPDA-PDA PAE, 0.538 dl/g for PMDA-PDA PAA, 0.576 dl/g for PMDA-BZ PAA, 0.601 dl/g for PMDA-ODA PAA and 0.683 dl/g for BPDA-PDA PAA.

All precursor solutions with a concentration of 10–20 wt%, which were filtered with silver-membrane filters of 1.0 μm pore size, were spin-coated on silicon wafers and soft-baked at 80°C for 1 h. The soft-baked precursors were thermally imidized in an oven under a nitrogen atmosphere by a four-step imidization protocol: 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/60 min. The ramping rate of each step was 2.0K/min and the cooling rate was 1.0K/min. Using an alpha-stepper (Tencor Instrument), the thickness of polyimide films was measured to be 6.3–13.5 μm. Polyimide films were taken off from the substrates with the aid of distilled water and cut into specimens of 12 $\times$ 15 mm, followed by drying in a high vacuum of 10^{-6} torr for two–three days prior to use.

For polyimide films, water sorption isotherms were measured in 100% relative humidity (RH) at 25°C using a Cahn electrobalance (Model D-200), as described previously in the literature [11,12]. In addition, wide-angle X-ray diffraction (WAXD) measurements were conducted in the $\theta/2\theta$ mode over $2° < 2\theta < 80°$ using a Rigaku diffractometer with a β-filtered CrK_α radiation source. One half degree defining and scatter slits were used together with a 0.3 mm receiving slit. Step and count data were taken at 0.02°(2θ) intervals at a scan speed of 0.4–1.0°/min. The measured WAXD patterns were corrected to the background run and then normalized for the film samples prepared from PAE and the corresponding PAA precursor by matching the integrated intensity over the range of 80–85°(2θ).

3. Results and discussion

The measured water sorption isotherms are shown in Fig. 2. These isotherms follow nearly Fickian process. Therefore, the isotherms were analyzed by the following

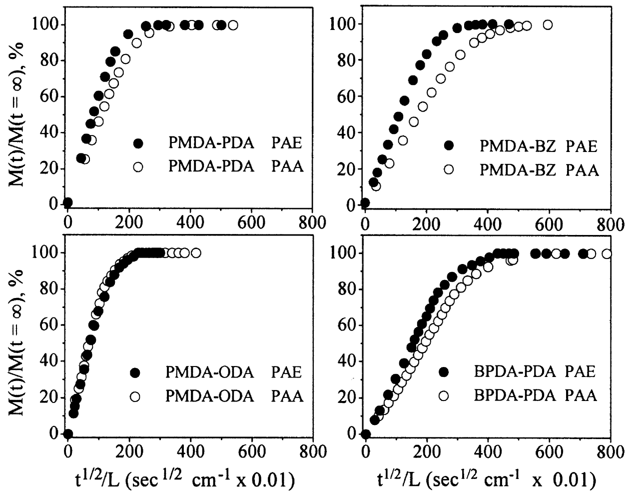

Fig. 2. Water sorption isotherms of polyimides in thin films prepared from their poly(amic diethyl ester) [PAE] and poly(amic acid) [PAA] precursors.

Table 1
Water diffusion coefficients and sorptions in thin films of polyimides prepared from poly(amic diethyl ester) [PAE] and poly(amic acid) [PAA] precursors[a]

Polyimide	Precursor origin	Film thickness L (μm)	Diffusion coefficient of water D, $\times 10^{-10}$ (cm^{2}s^{-1})	Water sorption at equilibrium $M(\infty)$ [wt%]
PMDA-PDA	PAE	13.50	7.30	5.90
	PAA	13.00	3.60	5.80
PMDA-BZ	PAE	7.50	3.40	3.30
	PAA	6.30	1.65	2.67
PMDA-ODA	PAE	12.47	9.00	2.60
	PAA	12.77	10.50	2.50
BPDA-PDA	PAE	12.11	2.20	1.90
	PAA	12.43	1.40	1.30

[a] Measured at 100%RH and 25°C.

equation, which has been derived for an infinite slab with a constant surface concentration [13]:

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

where $M(t)$ is the water sorption at a time t, $M(\infty)$ the water sorption at $t = \infty$, D the diffusion coefficient of water and L the film thickness. The results are summarized in Table 1.

For rodlike PMDA-PDA, the diffusion coefficient of water (D) in the film prepared from the PAE precursor (i.e. the PAE-derived polyimide film) is almost twice as high as that of the film obtained from the PAA precursor (i.e. the PAA-derived polyimide film). A similar effect of precursor origin on the water diffusion was observed for the rodlike PMDA-BZ and pseudo-rodlike BPDA-PDA polyimide. In contrast, for semi-flexible PMDA-ODA, the PAE-derived polyimide film exhibited a relatively lower D than that of the corresponding PAA-derived polyimide film. However, water sorption at the equilibrium [$M(\infty)$] was always slightly higher in the PAE-derived polyimide film than the PAA-derived polyimide film, regardless of the polymer backbone structure.

The effects of precursor origins on the water diffusion and sorption behaviors might result from some differences in the morphological structures of polyimide films prepared from the PAE and PAA precursors. Some information about the morphological structures can be obtained from WAXD patterns of the polyimides shown in Fig. 3. For all the polyimides in thin films, (00l) diffraction peaks, which correspond to the molecular order along the chain axis, were observed only in the transmission pattern. This indicates that for all the polyimides, polymer chains were preferentially aligned in the film plane, regardless of the precursor origin as well as the polymer backbone structure. However, the degree of molecular in-plane orientation is

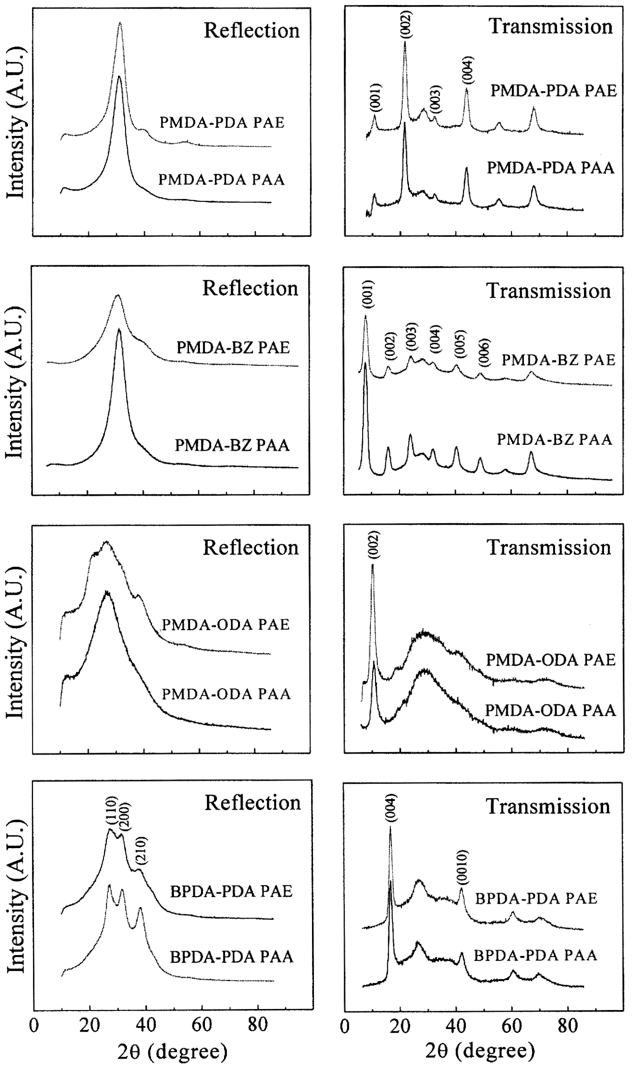

Fig. 3. WAXD patterns of polyimides in thin films prepared from their poly(amic diethyl ester) [PAE] and poly(amic acid) [PAA] precursors. WAXD patterns were measured in both reflection and transmission geometry. The CrK_α radiation source was employed.

dependent upon the precursor origin and polymer backbone structure. For PMDA-PDA, PMDA-BZ and BPDA-PDA, the degree of molecular in-plane orientation was relatively lower in the PAE-derived polyimide films than the PAA-derived polyimide films. However, for PMDA-ODA, the molecular in-plane orientation was higher in the film obtained from the PAE than that from the PAA.

For PMDA-PDA, the transmission pattern was apparently not influenced by the history of the precursor. Only the intensity of the diffraction peak at around 28.0° (2θ), which corresponds to the lateral packing of polymer chains in the film plane, was slightly enhanced for the PAE-derived polyimide film. This indicates that for the film from the PAE, the lateral packing of polymer chains in the film plane has been slightly improved in a regular way. From the diffraction peak, the mean intermolecular distance is calculated to be 4.63 Å (28.6°) for the PAE-derived polyimide film and 4.78 Å (27.7°) for the PAA-derived film. In contrast to the transmission pattern, the reflection pattern showed only three diffraction peaks related to the intermolecular packing without any regular order. For the PAE-derived polyimide, the first order amorphous halo appeared at 31.1°, giving a *d*-spacing of 4.27 Å. Also, the PAA-derived polyimide film showed an amorphous halo at 30.9° ($d = 4.30$ Å). The other two diffraction peaks at 39.2° and 54.9° are relatively stronger in the PAE-derived polyimide film than the PAA-derived film. However, the first order amorphous halo peak is relatively much sharper in shape and stronger in intensity for the PAA-derived polyimide film than the PAE-derived film. These results observed in this study are quite different from those reported previously by Goeschel et al. [14]. In conclusion, the polymer chains are more densely packed in the direction of film thickness than in the film-plane, regardless of the history of the precursor. In comparison, the overall population of the more ordered phase is relatively higher in the PAA-derived polyimide film than the PAE-derived film. However, the chain packing order in the more ordered phase is slightly better in the PAE-derived polyimide film than the PAA-derived film.

For PMDA-BZ, the PAA-derived polyimide film exhibited relatively sharper and stronger diffraction peaks than the PAE-derived film. In the transmission pattern, the mean intermolecular distance was 4.67 Å (28.4°) for the PAE-derived polyimide film and 4.64 Å (28.6°) for the PAA-derived film. In the reflection pattern, the mean intermolecular distance was 4.27 Å (31.1°) for the PAE-derived polyimide film and 4.23 Å (31.4°) for the PAA-derived film. That is, the polymer chains are more densely packed in the direction of film thickness than in the film-plane, regardless of the history of the precursor, as observed for the PMDA-PDA polyimide. Conclusively, both the population of the more ordered phase and the chain packing order are higher in the PAA-derived polyimide film than the PAE-derived polyimide film.

For the BPDA-PDA polyimide, known to be in the crystalline state based on the orthorhombic crystal unit cell with a space group of *Pba2* [7,15], the PAA-derived polyimide film revealed a higher intermolecular packing order and higher overall crystallinity than did the PAE-derived film, as shown in Fig. 3. This result is also quite different from that reported by Goeschel et al. [14]. A *d*-spacing of (110) diffraction, which gives information about the intermolecular distance, was 4.92 Å (26.9°) in the transmission pattern and 4.83 Å (27.4°) in the reflection pattern, regardless of the precursor origin.

As described above, for PMDA-PDA, PMDA-BZ and BPDA-PDA, PAA precursors produced better intermolecular order and higher population of the more ordered phase in the resultant polyimide films than did the corresponding PAE precursors. These morphological differences might be reflected directly on the water diffusion and sorption, consequently leading to a relatively greater rapid water diffusion and slightly higher water sorption in the PAE-derived polyimide films than the PAA-derived films.

However, for PMDA-ODA, the PAE precursor produced a relatively better intermolecular packing order in the resultant polyimide film than did the corresponding PAA precursor (see Fig. 3). However, the mean intermolecular distance was 5.11 Å (25.9°) in the transmission pattern and 4.92 Å (26.9°) in the reflection pattern, regardless of the history of the precursor. From this morphological information, one can expect that the PAE-derived polyimide film reveals a slower water diffusion and a lower water sorption than the PAA-derived film. The measured water diffusions are in agreement with the prediction. However, the water sorption was slightly higher in the PAE-derived polyimide film than the PAA-derived film.

In comparison, for the PAE-derived polyimide films, as well as the PAA-derived polyimide films, the diffusion coefficients of water *D*s are in the decreasing order PMDA-ODA > PMDA-PDA > PMDA-BZ > BPDA-PDA, respectively (see Table 1). In addition, the water sorptions $M(\infty)$s are in the decreasing order PMDA-PDA > PMDA-BZ > PMDA-ODA > BPDA-PDA, respectively. This result might be attributed to at least two contributory factors, chemical affinity to water and morphological structure. Regarding chemical backbones, the chemical affinity to water is in the decreasing order PMDA-ODA > PMDA-PDA > PMDA-BZ~BPDA-PDA [16–18]. The mean intermolecular distance, as a morphological factor, is in the decreasing order PMDA-ODA > BPDA-PDA > PMDA-PDA~PMDA-BZ. The overall population of the more ordered phase in the polyimide film is in the increasing order PMDA-ODA~PMDA-PDA~PMDA-BZ < BPDA-PDA. Therefore, the diffusion coefficients of water in the polyimide films are in good agreement with the prediction based on both the chemical affinities to water and the overall population of the more ordered phase. However, the water sorptions in the polyimides do not follow this prediction. In particular, both PMDA-PDA and PMDA-BZ exhibited relatively high water sorptions in spite of their relatively low chemical affinities to water and small mean intermolecular distance, compared to PMDA-ODA. These may be attributed to high levels of morphological defects, e.g. relatively large-scaled free-volume and voids possibly formed by the insufficient chain mobilities due to their rodlike chain characteristics during the thermal imidization.

4. Conclusions

Both water diffusion, sorption behaviors and morphological structures in rodlike and semiflexible polyimides were found to be influenced by the history of the precursor origins, poly(amic diethyl ester) [PAE] and poly(amic acid) [PAA]. For all the polyimides except PMDA-ODA, the PAE-derived polyimide films revealed relatively poor intermolecular packing order and lower population of the more ordered phase than the corresponding PAA-derived films. However, for PMDA-PDA, the intermolecular packing order in the more ordered phase was slightly better in the PAE-derived film than the PAA-derived film. For PMDA-ODA, the PAE-derived film showed a relatively better intermolecular packing order and higher population of more ordered phase than the PAA-derived film.

These morphological variations due to the precursor origins might be reflected directly in the water diffusion and sorption behaviors. For all the polyimides, the water sorption was higher in the PAE-derived films than the PAA-derived films. For rodlike PMDA-PDA and PMDA-BZ, and pseudo-rodlike BPDA-PDA, the PAE-derived polyimide films exhibited almost twice as high as diffusion coefficients of water than those of the corresponding PAA-derived polyimide films. However, for semiflexible PMDA-ODA, the PAE-derived polyimide film revealed a slightly lower diffusion coefficient of water and slightly higher water sorption than those of the PAA-derived film. Overall, the effect of the precursor origin on the water diffusion and sorption is significantly high in the rodlike or pseudo-rodlike polyimides having a high chain rigidity and high intermolecular packing order, but relatively low in the semiflexible polyimide with a relatively low chain rigidity.

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