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Moisture-induced stress relaxation of polyimide thin films

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Abstract

Four different polyimides: rodlike poly(*p*-phenylene pyromellitimide) (PMDA-PDA), pseudo-rodlike poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA), semiflexible poly(4,4-oxydiphenylene pyromellitimide) (PMDA-ODA) and poly(4,4-oxydiphenylene biphenyltetracarboximide) (BPDA-ODA) were prepared from two different precursors, poly(amic diethyl ester) (PAE) and poly(amic acid) (PAA). For polyimides prepared from the PAE precursors, stress relaxation coefficient at 25°C, 100% RH was 14.76×10^{-10} cm^2/s for PMDA-PDA, 3.29×10^{-10} cm^2/s for BPDA-PDA, 24.91×10^{-10} cm^2/s for PMDA-ODA and 9.34×10^{-10} cm^2/s for BPDA-ODA. For polyimides prepared from the PAA precursors, stress relaxation coefficient at 25°C, 100% RH was 10.50×10^{-10} cm^2/s for PMDA-PDA, 1.91×10^{-10} cm^2/s for BPDA-PDA, 28.84×10^{-10} cm^2/s for PMDA-ODA and 9.10×10^{-10} cm^2/s for BPDA-ODA. The effect of bulky ethyl ester group on the stress relaxation behavior is significantly high in rodlike PMDA-PDA or pseudo-rodlike BPDA-PDA having high chain rigidity and intermolecular packing order. The decreased birefringence, crystallinity and the looser packing in amorphous region of rigid polyimide derived from PAE may induce fast stress relaxation compared to flexible polyimide. Specially, the different chain mobility of polyimide also induced significant effect on the stress relaxation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Stress relaxation; Morphology; Chain mobility

1. Introduction

Future multichip packing technologies are expected to benefit from the use of polymers as interlayer dielectrics, 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]. One polyimide precursor is poly(amic acid) (PAA), which is synthesized in an aprotic solvent from the polycondensation of dianhydride and diamine monomers. Another polyimide precursor is poly(amic dialkyl ester) (PAE). It has increased hydrolytic stability in solution, improved solubility and higher imidization temperature regime that offers a wider processing window for good adhesion [4,5]. Thus, poly(amic dialkyl ester) as a polyimide precursor may be more adequate for fabrication in the microelectronics industry.

However, the properties of the polyimide derived from a PAE were different from those of the polyimide from a PAA, even though they have identical chemical backbone by the conventional thermal baking [6–9]. Outgassing of ethyl groups and package components depends strongly upon the imidization condition as well as boiling points and degradation temperatures. Even though ethyl groups are fully outgassed, they influence the morphological structure of the precursor in the condensed state as well as imidization kinetics, consequently leading to different structure and properties in the resultant polyimide.

Polyimide materials posing significant problems due to their inherent time-dependence and susceptibility to the moisture-induced stress relaxation characteristics are an interesting subject matter to be investigated. Water causes metal corrosions, failures of the adhesion to metals and degradation of dielectric properties when exposed to air [10,11]. Besides, the dimension of imide films will be affected by water due to swelling.

The water sorption behavior of polyimide-PAA-derived films has been extensively studied using gas permeation analyzer [12,13], electro-microbalance [14–17], residual stress analyzer [18,19] and capacitance tester [20]. These fairly report that diffusion constants relate with the packing coefficient, chemical structure of imide molecule and the morphology of imide film. Jou et al. [18] have studied the effect of structure on water diffusion and hygroscopic stress in the polyimide films using a bending beam method. They found that the diffusion of water in polyimide films obey Fick’s law. Later, Han et al. [14–17] also found, using a

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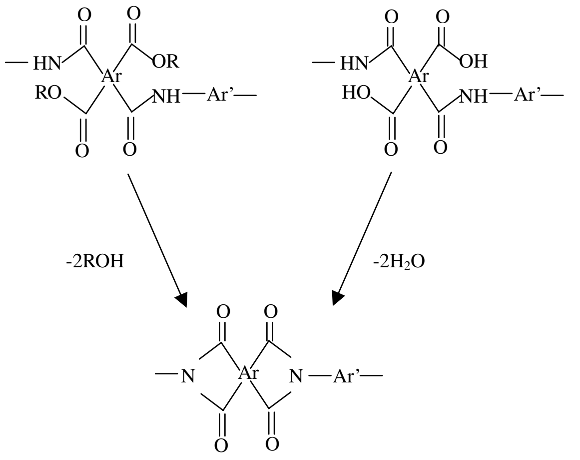

Fig. 1. Polyimides prepared from PAE and PAA precursors by thermal imidization, R is ethyl.

gravimetric method with electro-microbalance, that water sorption in polyimide films was influenced by in-plane orientation, chain order and thickness. In addition, the diffusion coefficients of water sorption in some of the polyimides prepared from functionalized PAAs were estimated from the residual stress relaxation behavior. Also, water diffusion behavior was used to compared the results of water sorption by the gravimetric method to the results by stress relaxation method [19,21]. However, moisture-induced stress relaxation in PAE-derived film has been rarely understood with morphological structure.

Therefore, PAEs of four different polyimides with various chain rigidities were synthesized (Fig. 1). The stress relaxation in the films adhered to silicon substrates was measured using a thin film stress analyzer (TFSA) at 25°C in 100% relative humidity and analyzed by the Fickian process. Stress relaxation was interpreted by the consideration of the morphological structure and chain mobility depending on precursor origin. Here, in the course of water sorption, stress reduction is measured by radius of curvature change of polyimide/Si curvature. Therefore, this kind of stress may be called mean position-averaged stress. For the characteristic properties of polyimide thin films, morphological structures were examined using wide-angle x-ray diffraction (WAXD) and prism coupler, for the chain mobility using dynamic mechanical thermal analyzer (DMTA) and thermal stability by thermal gravimetric analysis (TGA).

2. Experimental

2.1. Material and sample preparation

Poly(*p*-phenylene pyromellitamic diethyl ester) (PMDA-PDA PAE) was synthesized by the low-temperature polymerization of *p*-phenylene and pyromellitic diethyl ester diacyl in dry *N*-methyl-2-pyrrolidone (NMP) [22,23]. The precursor polymer solution was precipitated in deionized water, filtered and washed by methanol to remove HCl byproducts. The precursor was dried for 2 days at 50°C in a vacuum oven. The other poly(amic diethyl ester)s were prepared in the same method as PMDA-PDA PAE was: poly(*p*-phenylene biphenyltetracarboxamic diethyl ester) (BPDA-PDA PAE), poly(4,4′oxydiphenylene pyromellitamic diethyl ester) (PMDA-ODA PAE) and poly (4,4′oxydiphenylene biphenyltetracarboxamic diethyl ester) (BPDA-ODA PAE). The corresponding PAAs were synthesized in dry NMP from the respective dianhydrides and diamines: poly(*p*-phenylene pyromellitamic acid) (PMDA-PDA PAA), poly(*p*-phenylene biphenyltetracarboxamic acid) (BPDA-PDA PAA), poly(4,4′ oxydiphenylene pyromellitamic acid) (BPDA-PDA PAA) and poly(4,4′oxydiphenylene biphenyltetracarboxamic acid) (BPDA-ODA PAA). All precursor solutions with concentration of 12–15 wt.% were spin-coated on silicon wafers and soft baked at 80°C for 1 h. The stress relaxation behavior of polyimide films was measured using TFSA after conventional thermal imidization from 25 to 400°C. The ramping rate was 2.0°C/min and cooling rate was 1.0°C/min. To exclude thickness effect, the thickness of polyimide films were controlled in the range of 9–11 μm using spin coater, and measured using an Alpha-stepper (Model 2000, Tencor Instruments).

2.2. Measurement

To determine residual stress from the measured radii of curvature, the well known Eq. (1) was employed [24]. Residual stress was calculated from the measured radii of curvature using the following equation

$$\sigma = \frac{E_{\mathrm{s}}}{6(1-\nu_{\mathrm{s}})}\frac{t_{\mathrm{s}}^2}{t_{\mathrm{f}}}\left(\frac{1}{R_2}-\frac{1}{R_1}\right) \tag{1}$$

σ is residual stress in polyimide film. The subscripts, f and s denote polyimide film and substrate, respectively. E, ν and t are Young's modulus, Poisson's ratio and thickness, respectively. R_1 and R_2 are, respectively, wafer curvatures measured before and after film deposition. For Si(100) wafer, $E_{\mathrm{s}}/(1-\nu_{\mathrm{s}})$ is 180 500 MPa [25]. Before use, the initial curvature and thickness of wafers were measured using TFSA and a thickness gauge (SM1201, Teclock Co., Japan).

Stress relaxation due to water diffusion can be determined by the measuring the stress difference as a function of time. The film stress relaxation at a highly supercooled state is predominated by the moisture uptake in a humid environment [19]. Here, the stress relaxation is caused from the moisture so that the rate of stress reduction may reflect that of water absorbed by the film. Therefore, for films in which the moisture uptake obeys Fick's law, the stress relaxation rate can be estimated by best-fitting the moisture-induced stress relaxation versus time curves. Thus, the stress relaxation of polyimide thin film can be expressed quantitatively from a macroscopic viewpoint by Fick's

Table 1
Stress relaxation behavior of polyimides prepared from PAE and PAA precursors

Polyimide		Thickness (μm)	Residual stress σ_I (MPa)	Residual stress σ_f (MPa)	Relaxed stress ($\Delta\sigma$)	Relaxation coefficient, S[a] ($\times 10^{-10}$ cm^2/s)
PMDA-PDA	PAA	11	−5.1	−15.0	9.9	10.50
	PAE	11	13.4	−0.6	14.0	14.76
BPDA-PDA	PAA	9	7.0	2.3	4.7	1.91
	PAE	11	19.5	12.2	7.3	3.29
PMDA-ODA	PAA	10	29.4	21.7	7.7	28.84
	PAE	11	30.3	21.9	8.4	24.91
BPDA-ODA	PAA	9	40.1	31.9	8.2	9.10
	PAE	10	39.5	23.7	10.3	9.34

[a] Estimated from the stress relaxation behavior at 25°C, 100% RH.

laws of diffusion [26–28]. If $\sigma_\mathrm{w}(t)$ is the stress induced by water diffusion at time t and $\Delta\sigma$ is the difference between the stresses at $t = 0$ and $t = \infty$, then Eq. (2) gives the time dependence of stress in terms of the stress relaxation coefficient (S) and thickness (L) of thin film

$$\frac{\sigma_0 - \sigma_\mathrm{w}(t)}{\Delta\sigma} = 1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\exp\left[-\frac{\pi^2(2n-1)^2}{4L^2}St\right] \tag{2}$$

The experimental data was plotted with stress relaxation ratio $(\sigma_0\sigma_\mathrm{w}(t))/\Delta\sigma$ as a function of $t^{1/2}L^{-1}$. Using Eq. (2), various values of S were assumed, and the error between experiment and relaxation was minimized to produce the fitted apparent stress relaxation coefficient (S).

For WAXD measurements, fully cured films were removed from substrate after soaking in distilled water for 24 h. WAXD measurements were conducted in the $\theta/2\theta$ method over 3.5–60° using a Rigaku diffractometer (Model D/Max-200B) with CuKα ($\lambda = 1.54$ Å) radiation source. Step and count data were taken at 0.02° intervals at a scan speed of 0.4°/min. Measured WAXD was corrected to the background run and then normalized for the film samples prepared form PAE and the corresponding PAA precursor by matching integrated intensity over the range 58–60° (2θ) [29,30].

For birefringence of polyimides films, prism coupling patterns were measured using a Metricon prism coupler (Model 2010). The refractive index in the film plane, n_{xy} was measured in the TE mode, n_z was measured in the TM mode as described elsewhere [17–20]. All measurements were performed using a cubic zirconia prism of $n_\mathrm{TE} = n_\mathrm{TM} = 2.1677$ at a wavelength of 632.8 nm. The birefringence ($\Delta = n_{xy} - n_z$) is a measure of the molecular orientation in the in-plane of the polyimide thin film.

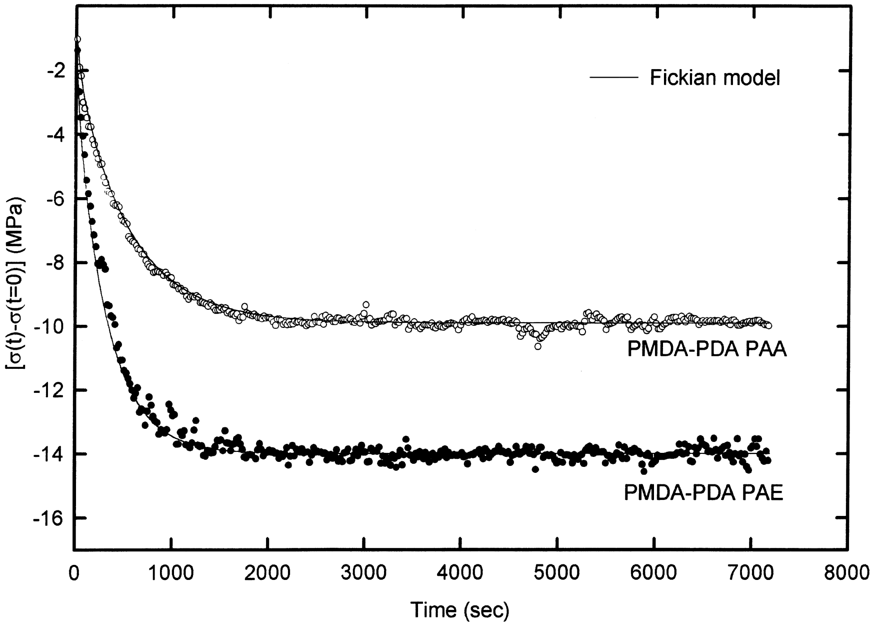

Fig. 2. Isotherms of stress relaxation of PMDA-PDA polyimide thin films prepared from PAE and PAA.

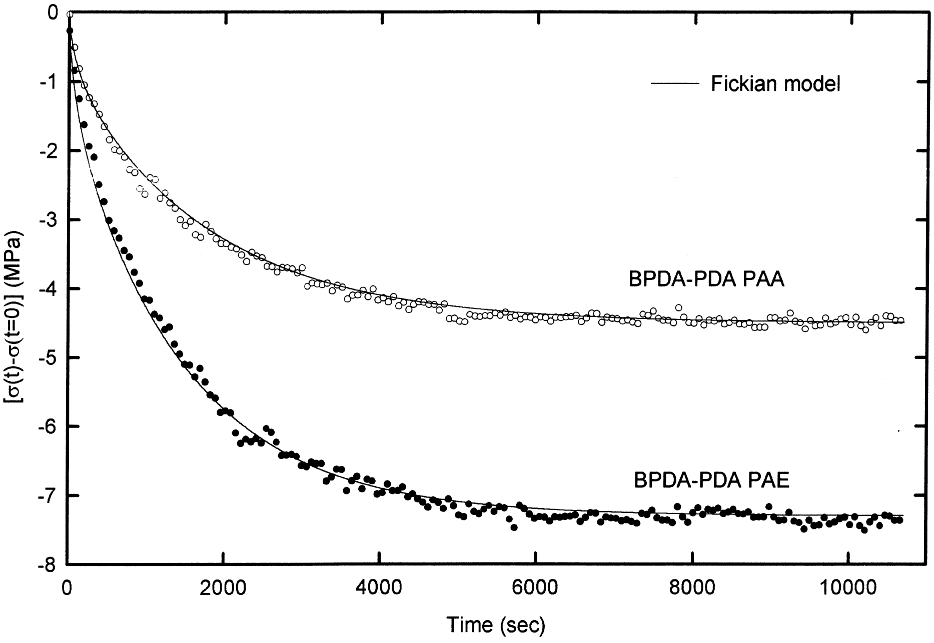

Fig. 3. Isotherms of stress relaxation of BPDA-PDA polyimide thin films prepared from PAE and PAA.

For thermal properties of polyimide films during thermal imidization, DMTA (Polymer Lab. MKIII) was used. The heating rate and frequency were 5.0°C/min and 1 Hz, respectively. In addition, thermal stability depending on precursor origins was examined on a DuPont TG/DSC thermogravimetric analyzer. Heating rate was 10°C/min under nitrogen atmosphere.

3. Results and discussion

Stress relaxation isotherms of PAA and PAE thin films were investigated at 25°C and 100% relative humidity as shown in Table 1. Cured polyimide films on the substrate always exhibited residual stress, which may be tensile or compressive. When uptaking water, stress relaxation

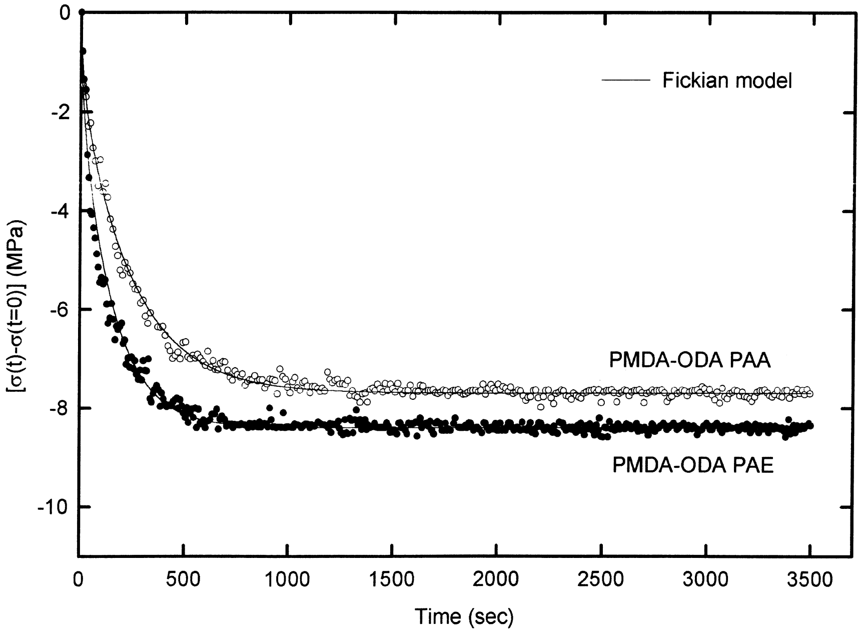

Fig. 4. Isotherms of stress relaxation of PMDA-ODA polyimide thin films prepared from their PAE and PAA.

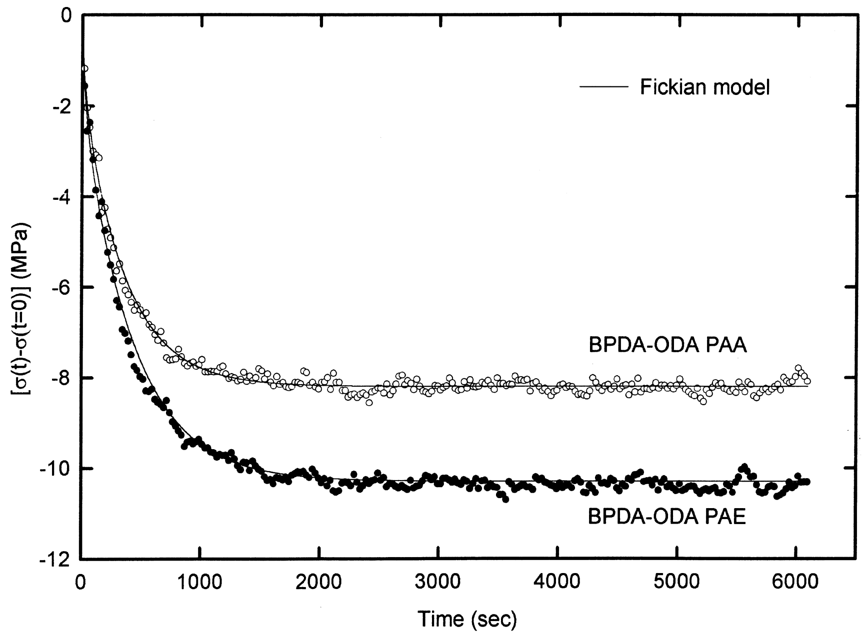

Fig. 5. Isotherms of stress relaxation of BPDA-ODA polyimide thin films prepared from their PAE and PAA.

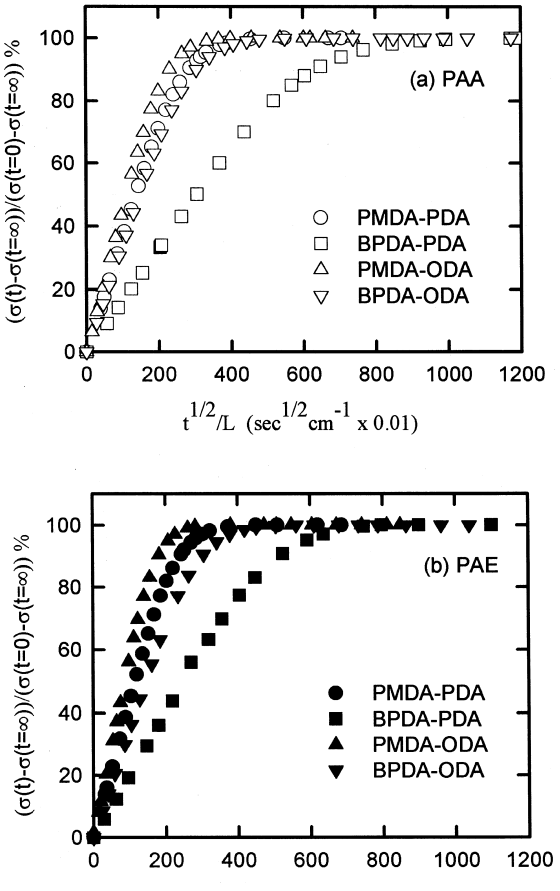

Fig. 6. Isotherms of stress relaxation in the films of various polyimides fitted by Fick's law at 25°C, in 100% RH: (a) PAA; and (b) PAE.

isotherms of polyimide films apparently followed the Fickian process. In addition, the compressive phenomenon was found due to be stress relaxation induced by water diffusion into polyimide thin films.

The equilibrium stress reduction was 9.9 MPa for PMDA-PDA PAA and 14.0 MPa for PMDA-PDA PAE. For BPDA-PDA, residual stress reduction was 4.8 MPa for the PAA and 7.3 MPa for the PAE. The stress reduction for rodlike PMDA-PDA and pseudo-rodlike BPDA-PDA-derived PAE precursor is quite higher than that of the polyimide prepared from the respective PAAs as shown in Figs. 2 and 3. These indicate that moisture-induced stress relaxation behavior of the pseudo-rodlike BPDA-PDA and rodlike PMDA-PDA polyimide is sensitive to precursor origin.

The equilibrium stress reduction in semi-flexible PMDA-ODA was in the 7–8 MPa range as shown in Fig. 4. For BPDA-ODA prepared from PAA and PAE precursor, the equilibrium stress reduction induced by water diffusion was 8.2–10.3 MPa, as shown in Fig. 5. As observed in Figs. 3 and 4, semiflexible PMDA-ODA and BPDA-ODA did not show significant dependency, in contrast to both rodlike PMDA-PDA and pseudo-rodlike BPDA-PDA. It indicates that the effect of diethyl groups may be insensitive to stress relaxation in the flexible polyimide. In other words, a polyimide having hinged linkage is relatively insensitive to stress relaxation due to water diffusion. This suggests that the stress relaxation of polyimide film is highly related to morphological structure.

The stress relaxation rates were also summarized in Table 1. It was 10.50×10^{-10} cm^2/s for the PMDA-PDA PAA and 14.76×10^{-10} cm^2/s for the PMDA-PDA PAE. The rodlike PMDA-PDA polyimide prepared from the PAE precursor shows faster stress relaxation rate (*S*) than the PAA-derived

Table 2
Mean intermolecular distances and coherence length in thin films of polyimides

Polyimide	Mean intermolecular distances[a]		Coherence length (Å)[b]	Film thickness (μm)
	In-plane[c] (Å)	Out-of-plane[d] (Å)		
PMDA-PDA (PAA)	4.71	4.25	130	11
PMDA-PDA (PAE)	4.72	4.29	120	11
BPDA-PDA (PAA)	4.82	4.73	123	9
BPDA-PDA (PAE)	4.82	4.73	118	11
PMDA-ODA (PAA)	4.92	4.72	80	10
PMDA-ODA (PAE)	4.91	4.71	85	10
BPDA-ODA (PAA)	4.80	4.80	–	9
BPDA-ODA (PAE)	4.80	4.80	–	10

[a] Estimated from the maximum of X-ray diffraction peaks corresponding to the intermolecular spacing.
[b] Calculated from the peak maximum of (00*l*) peak in transmission WAXD patterns.
[c] Calculated from the peak maximum of amorphous halos in transmission WAXD patterns.
[d] Calculated from the peak maximum of amorphous halos in reflection WAXD patterns.

ones. A similar effect of precursor origin on the stress relaxation was observed for pseudo-rodlike BPDA-PDA polyimide. Those were 1.91×10^{-10} cm^2/s for the BPDA-PDA PAA and 3.29×10^{-10} cm^2/s for BPDA-PDA PAE at 25°C and 100% RH, respectively. This may indicate that the water molecule diffuses more quickly into the PAE-derived film than the PAA-derived thin film.

However, the effect of precursor origin on the stress relaxation coefficient for semi-flexible PMDA-ODA and BPDA-ODA is relatively insignificant. It was 28.84×10^{-10} cm^2/s for the PMDA-ODA PAA and 24.91×10^{-10} cm^2/s for PMDA-ODA PAE at 25°C, 100% RH. PMDA-ODA polyimide did not show any strong dependency of the precursor origin on stress relaxation rate, compared to rodlike PMDA-PDA and pseudo-rodlike BPDA-PDA. Here, the PAE-derived polyimide film exhibited slightly slower stress relaxation than the corresponding PAA-derived film. Stress relaxation rate at 25°C, 100% RH was about 9×10^{-10} cm^2/s for BPDA-ODA films regardless of precursor origin. As observed for the semiflexible PMDA-ODA polyimide, BPDA-ODA polyimide did not show significant dependency of the precursor.

As shown in Fig. 6, stress relaxation rate using Fickian diffusion model varies in the range of 1.91×10^{-10} to 28.84×10^{-10} cm^2/s for PAA-derived films and 3.29×10^{-10} to 24.91×10^{-10} cm^2/s for PAE-derived films. Stress relaxation rate in polyimide prepared from PAE precursor was faster than that of the corresponding polyimide except for PMDA-ODA thin films. In addition, rodlike PMDA-PDA revealed relatively slow relaxation rates in spite of highest stress reduction. These indicate that the stress relaxation behavior induced by water diffusion might result from differences in the morphological structures in polyimide films prepared from PAE and PAA precursors.

Morphological structure of polyimide thin films was previously investigated using WAXD [8,9,31,32]. The transmission pattern of PMDA-PDA apparently shows multiple diffraction peaks from high ordering along the chain axis. However, it exhibits only an amorphous halo peak in the reflection. This indicates that PMDA-PDA chains are mainly oriented and highly ordered in the film plane due to rodlike chain nature, but irregularly packed together in the out of film plane. Specially, the PAA-derived polyimide film exhibited relatively sharper and stronger diffraction peaks than did the PAE-derived film. Mean

Table 3
Optical properties in thin films of polyimides

Polyimide	Refractive index		Birefringence	Film thickness (μm)
	In-plane (n_{xy})	Out-of-plane[a] (n_z)		
PMDA-PDA (PAA)	1.8202	1.5902	0.2300	11
PMDA-PDA (PAE)	1.8045	1.5991	0.2054	11
BPDA-PDA (PAA)	1.8501	1.6127	0.2374	9
BPDA-PDA (PAE)	1.8266	1.6263	0.2033	11
PMDA-ODA (PAA)	1.7168	1.6409	0.0759	10
PMDA-ODA (PAE)	1.7171	1.6411	0.0760	10
BPDA-ODA (PAA)	1.6936	1.6719	0.0217	9
BPDA-ODA (PAE)	1.6934	1.6712	0.0213	10

[a] Measured at 632.8 nm (i.e. 474.08 THz).

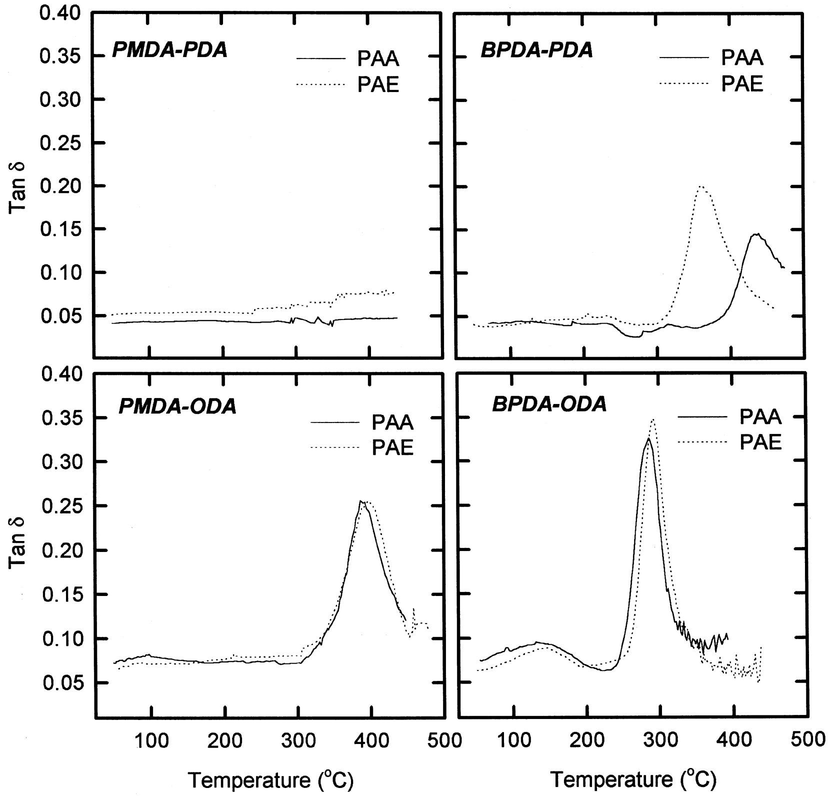

Fig. 7. Variation of dynamic tan δ with temperature in various PAA-derived films and PAE-derived films.

intermolecular distance in the film plane was estimated from diffraction peak of the amorphous halo in the transmission pattern as shown in Table 2.

This shows 4.71 Å (19.03°) for the PAE-derived polyimide film and 4.72 Å (18.77°) for the PAA-derived film. Mean intermolecular distance in the out-of-plane was 4.25 Å (20.88°) for the PAA-derived film and 4.29 Å (20.69°) for the PAE-derived film. This may indicate relatively coarse molecular packing in the amorphous phase of the PAE-derived film. In addition, the chain anisotropy of polymer chains estimated from birefringence was also detected using prism coupler, in the refractive index measurements, as shown in Table 3. The PMDA-PDA prepared from PAA revealed an in-plane refractive index (n_{xy}) of 1.8202 and an out-of-plane refractive index (n_z) of 1.5902, giving a relatively high birefringence (Δ) of 0.2300. On the other hand, a film derived from PAE showed 1.8045 (n_{xy}) and 1.5991 (n_z), respectively, resulting in 0.2054 (Δ). It indicates that chain anisotropy of PMDA-PDA is more favorable in the PAA film. Therefore, the higher chain anisotropy might lead to the lower stress relaxation rate.

For BPDA-PDA polyimide, multiple (00*l*) peaks also appeared only in the transmission [8,9]. It indicates that the polyimide molecules ordered highly along chain axis are preferentially aligned in the film plane. The PAA-derived film revealed higher intermolecular packing order and overall crystallinity than that did the PAE-derived film, as observed for the PMDA-PDA film. This was evident in the refractive index measurements. As shown in Table 3, birefringence was decreased to 0.2033 in the PAE film from 0.2374 in the PAA film. It indicates that high in-plane orientation was degraded somewhat in the PAE-derived film. However, the mean intermolecular distance was 4.82 Å (18.39°) in the transmission pattern and 4.73 Å (18.75°) in the reflection pattern, regardless of precursor origin.

For rodlike PMDA-PDA and pseudo-rodlike BPDA-PDA, PAA precursors produced better chain rigidity and higher population of more ordered phase in the resultant polyimide film than the corresponding PAE precursors. Generally water diffusion probably occurs in the amorphous region with looser molecular packing. PAE indeed leads to lower crystallinity and, simultaneously, to looser molecular packing in the amorphous region in WAXD. This suggests that disrupted chain order in the PAE-derived polyimide thin film leads to a higher stress relaxation rate (*S*) than the PAA-derived films. Also, it is suggested that the variations in the molecular order and orientation caused by the ethyl ester group are the important factors to moisture-induced stress relaxation behavior in the PAE-derived polyimide.

PMDA-ODA exhibited a sharp diffraction peak at the low angle region corresponding to chain order along the chain axis and a large amorphous halo in the transmission peak [8,9]. In addition, it showed only a large amorphous halo peak in the reflection pattern. This means that PMDA-ODA has some chain order along the chain axis, but is irregularly packed in the direction of film thickness. The PAE precursor produced a relatively better intermolecular order in the resultant polyimide film than the corresponding PAA precursor. The increased intensity (002) peak in the transmission confirms increase in the in-plane orientation with the PAE-derived film. The in-plane orientation was also evident in the birefringence. It was 0.0759 for the PAA and 0.0760 for the PAE. The mean intermolecular distances were similar depending on precursor type; 4.91 Å in the film plane and 4.71 Å in the out-of-plane for the PAE, whereas for the PAA-derived polyimide, 4.92 Å, in the film plane and 4.72 Å in the out-of-plane. From this morphological information, it may be expected that PAE-derived polyimide films show slightly slower stress relaxation than the PAA-derived films.

The effect of ethyl ester group was nearly negligible in the structure of BPDA-ODA. Regardless of precursor origin, BPDA-ODA revealed crystalline-like diffraction with a large amorphous halo [8,9]. The absence of (00*l*) peak in the transmission for others polyimides, is evidence by the fact that polymer chains are randomly aligned in the film plane. In addition, films were weakly anisotropic in the chain orientation, leading to the weak birefringence of 0.0217–0.0213. Mean molecular distances were roughly estimated from diffraction patterns. It was 4.80 Å in the film plane as well as the out-of-plane regardless of precursor origin. As described above, evaporating the ethyl ester group during thermal curing process did not significantly vary molecular ordering in BPDA-ODA as well as PMDA-ODA. This is in good agreement with the stress relaxation rate due to water diffusion in the polyimide thin films based on morphological structure.

For the PAE-derived polyimide films as well as the PAA-derived polyimide films, PMDA-PDA showed the highest in-plane orientation and the lowest mean intermolecular distance. However, the pseudo-rodlike BPDA-PDA with the highest molecular packing order exhibits the lowest stress relaxation rate. This indicates that the molecular packing order as well as in-plane orientation are also important to the degree of stress relaxation due to water diffusion.

As an additional factor influencing stress relaxation induced by water diffusion, chain mobility could be considered as a key factor according to imidization temperature. During thermal imidization, the by-product groups debond from the precursor polymer and then evaporate. Through this evaporation process, microvoids may be generated in the resulting film. Spontaneously, they may be healed to a certain extent by chain mobility at the high temperature. Chain mobility is directly related to the T_g in polyimide. T_g‘s of the polyimide were examined and are shown in Fig. 7. In this study, tan δ profiles were used for estimating chain mobility depending on imidization temperature because they include the expression of dynamic loss modulus and show clear peak. The ethyl ester groups slightly affect the tan δ profiles for the polyimides. From the tan δ profiles, T_g was estimated to be 430°C for BPDA-PDA PAA, 380°C for BPDA-PDA PAE, 400°C for PMDA-ODA and 290°C for BPDA-ODA, regardless of precursors. The tan δ curve of BPDA-ODA showed a sharp glass transition, whereas the other polyimides relatively exhibited broad transition. It was in good agreement with the absence of the (00*l*) peak due to intrinsically amorphous structure in the polyimide thin films based on the morphology.

PMDA-PDA did not show glass transition over 50–450°C, indicating T_g is higher than 450°C, whereas the other polyimides showed one. During thermal imidization the imidized PMDA-PDA chains are immediately frozen because the T_g is higher than the final imidization temperature (400°C). Under this circumstance microvoids generated in thermal imidization process may not be healed completely. The limited chain mobility may contribute to the relatively high water uptaking site and then higher stress relaxation as shown in Fig. 2. Specially, due to highly limited chain mobility the effect of evaporating size in the precursor was significant in PMDA-PDA derived from PAE. It may induce a long intermolecular distance estimated from the peak of the amorphous halo compared to that of the PAA derived one.

Chain mobility depending on temperature is directly related to the tan δ curve. The tan δ is defined as the ratio of imaginary modulus (E'') divided by real modulus (E''). The real and imaginary moduli represent the elastic and viscous behavior of the polyimide, respectively. Thus, the increased area of the tan δ peak represents the increased viscous property and it is a very sensitive means of measuring glass transition. The magnitude of tan δ such as value and shape is due to both the backbone stiffness and the presence of crystallinity. The broad tan δ peak is attributed to semicrystalline morphology, whereas a narrow and prominent tan δ is characteristic of entirely amorphous polymers having high chain mobility.

In comparison to rodlike PMDA-PDA, pseudo-rodlike BPDA-PDA has a tan δ peak indicating glass transition. It means that BPDA-PDA has more mobility in the range of 300–450°C. However, the tan δ peak is broader and smaller than that of the semiflexible PMDA-ODA and BPDA-ODA, indicating that BPDA-PDA is less mobile. This broad and small tan δ peak is due to both higher chain rigidity and more presence of crystallinity. Chain mobility estimated from the tan δ curve of the polyimide films increase in the order, PMDA-PDA < BPDA-PDA < PMDA-ODA < BPDA-ODA during imidization up to 400°C. It is consistent with the results of morphological structure estimated by WAXD.

Depending on precursor origin in rigid polyimide such as PMDA-PDA and BPDA-PDA, the tan δ curve is lower or broader in films prepared from PAA- than PAE-derived film. The lower tan δ is induced from lower chain mobility. Thus, the limited chain mobility due to higher T_g and crystallinity in polyimide prepared from PAA may inhibit the sufficient moisture-induced stress relaxation. Thus, more or less high tan δ in PMDA-PDA and BPDA-PDA prepared

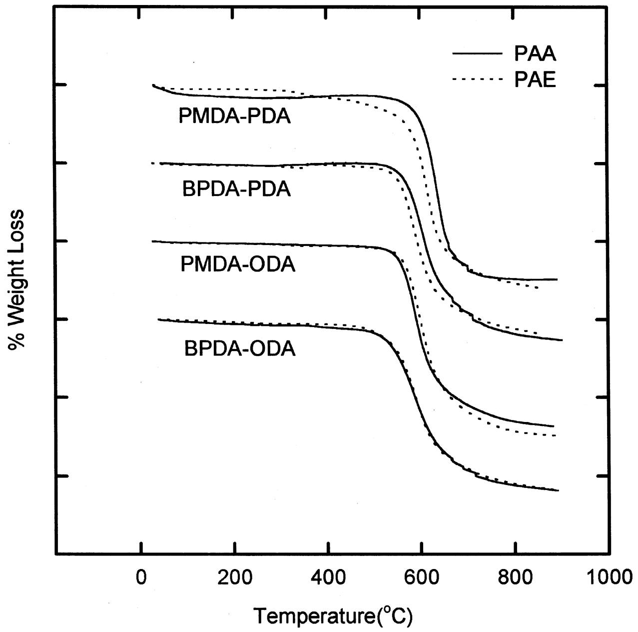

Fig. 8. Thermogravimetric analysis in various PAA-derived films and PAE-derived films.

from PAE leads to faster stress relaxation in fully cured polyimide thin films. However, for flexible polyimide such as PMDA-ODA and BPDA-ODA, the tan δ peak is relatively narrow, prominent and insensitive regardless of precursor origin, indicating that both PMDA-ODA and BPDA-ODA are relatively more flexible and insensitive to chain mobility. Here, microvoids generated by thermal imidization process might be healed completely. Thus, for both PMDA-ODA and BPDA-ODA, precursor effect might be not observed as readily on the stress relaxation induced by water diffusion. This shows a good agreement with results of moisture-induced stress relaxation and morphological structure of polyimide film.

The effect of diethyl ester precursor on the thermal stability was obtained by TGA from 25 to 900°C under nitrogen at a heating rate of 10°C/min in Fig. 8 and compared to that of PAA-derived polyimide films in Table 4.

The degradation step on the TGA curves all start at a temperature above 440°C. The temperatures at which 10% weight loss was observed lie in the range of 530–610°C, depending on the backbone chemistry. It was found that the degradation temperatures for the polyimides increased in the order PMDA-PDA > BPDA-PDA > PMDA-ODA > BPDA-ODA, regardless of precursor origin. This order is consistent with increasing molecular in-plane orientation of the polymer backbone. It may indicate that the chain orientation is one of the major factors controlling thermal stability. PMDA-PDA and BPDA-PDA, obtained from PAE precursor, exhibit a degradation onset temperature about 20°C lower than that obtained from the corresponding PAA-derived polyimide. Thus, the partially deteriorated chain orientation induced by the ethyl group may cause a decrease in the thermal stability, whereas that of both PMDA-ODA and BPDA-ODA with relatively low chain rigidity is little changed. This behavior appears to be also displayed in stress relaxation, WAXD and DMTA and hints at the importance of morphological structure.

Table 4
Characteristics of the thermal stability of the polyimide derived from both PAA and PAE precursors by thermal imidization at 400°C for 1 h

Polymer	Degradation onset (°C)	10 wt.% degradation (°C)
PMDA-PDA(PAA)	520	610
PMDA-PDA(PAE)	500	595
BPDA-PDA(PAA)	486	595
BPDA-PDA(PAE)	470	588
PMDA-ODA(PAA)	478	586
PMDA-ODA(PAE)	480	590
BPDA-ODA(PAA)	441	531
BPDA-ODA(PAE)	440	530

4. Conclusion

PAE precursors of four different polyimides; rodlike PMDA-PDA, pseudo-rodlike BPDA-PDA, semiflexible PMDA-ODA and BPDA-ODA were synthesized. TFSA has been successfully applied for the measurement of time-dependent stress relaxation in adhered film at 25°C in 100% relatively humidity. For polyimides prepared from the PAE precursors, stress relaxation (S) at 25°C, 100% RH was 14.76×10^{-10} cm^2/s for PMDA-PDA, 3.29×10^{-10} cm^2/s for BPDA-PDA, 24.91×10^{-10} cm^2/s for PMDA-ODA and 9.34×10^{-10} cm^2/s for BPDA-ODA. For polyimides prepared from the PAA precursors, stress relaxation at 25°C, 100% RH was 10.50×10^{-10} cm^2/s for PMDA-PDA, 1.91×10^{-10} cm^2/s for BPDA-PDA, 28.84×10^{-10} cm^2/s for PMDA-ODA and 9.10×10^{-10} cm^2/s for BPDA-ODA. For rigid polyimides such as PMDA-PDA and BPDA-PDA, the stress of PAE-derived polyimide films relaxed faster than the corresponding polyimides. However, for flexible polyimides such as PMDA-ODA and BPDA-ODA, the PAE-derived polyimides showed negligible effect on stress relaxation behavior. It was found that the effect of ethyl ester on stress relaxation is significantly high in the rodlike or pseudo-rodlike polyimides having high chain rigidity and a high intermolecular packing order, but relatively low in the semiflexible polyimide with relatively low chain rigidity. As shown in WAXD and refractive index analysis, the decreased crystallinity, in-plane orientation and the looser packing in amorphous region may primarily accelerate stress relaxation of polyimide derived from PAE. In addition, the effect of precursor origin on chain mobility and thermal stability was examined using DMTA and TGA, and showed consistent trends with morphological structure. The stress relaxation behavior induced by water diffusion was strongly affected by the nature of morphology, chain mobility during thermal imidization.

Acknowledgements

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