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Effects of Imide Structure/Thickness/Curing on Solvent Diffusions in Polyimides

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ABSTRACT: By the usage of a bending beam technique, it is found that the diffusion of NMP (*N*-methylpyrrolidone) solvent in PMDA–ODA (pyromellitic dianhydride–4,4′-oxydianiline) imide films belongs to case I diffusion, while that in PMDA–PDA (pyromellitic dianhydride–*p*-phenylenediamine) belongs to case II. The difference may presumably be attributed to the fact that PMDA–ODA is relatively flexible and can form an amorphous and large void-rich film structure so that NMP molecules can penetrate more freely, while PMDA–PDA is rigid and can form a highly crystalline and large void-free film structure so that NMP molecules need to relax the imide chain first in order for diffusion to proceed. The diffusion mechanisms do not vary with thickness ranging from 0.5 to 10 μm or curing temperature from 200 to 400 °C, while the diffusion processes apparently become faster with the increase of thickness and decrease of curing temperature. For PMDA–ODA cured at 250 °C, the calculated diffusion coefficient, D, increases from 1.2 to 3.7×10^{-11} cm^2/s for thickness increasing from 2.8 to 6.7 μm. For curing temperatures of 200, 250, 300, 350, and 400 °C, D = 4.8, 3.3, 1.8, 0.60, and 0.46×10^{-11} cm^2/s, respectively. For PMDA–PDA cured at 250 °C, the calculated diffusion front velocity, υ, increases from 2.6 to 14×10^{-8} cm/s for thickness increasing from 0.5 to 10.2 μm. For curing temperatures of 200, 250, 300, 350, and 400 °C, υ = 1.0, 0.70, 0.34, 0.23, and 0.099×10^{-7} cm^2/s, respectively. The increases in the diffusion rate with respect to increasing thickness and decreasing curing temperature may be attributed to the decrease in film ordering and/or orientation. The reversibility in the diffusion process upon repeated diffusion/drying cycles indicates that the films studied must be cross-linked. The degree of cross-linking seems to increase with the increase of film thickness.

Introduction

Polyimides are promising materials for microelectronic packaging applications for their excellent mechanical properties, low dielectric constant, high glass transition temperature, and high planarization characteristics.[1–9] In multichip module packaging, for example, structures with polyimide on polyimide are often encountered, wherein multiple polyimide layers are cast and cured alternately for a multilevel interconnection purpose.[2,8,9] For the structures, the strength of autohesion or adhesion of a given polyimide film on a prior cast and cured polyimide film having the same or different imide structure may become one of the major concerns regarding processing feasibility or device reliability.

As revealed by Brown et al.,[10] the strength of autohesion strongly depends on the depth of penetration of the later cast polyimide molecules into the prior cured film. This penetration process is made possible and should be lead by the occurrence of solvent-induced swelling in the prior film. In other words, the strength of polyimide–polyimide autohesion should be, in turn, governed by the diffusion of the solvent presented in the later applied film prior to solidifying upon prebaking and curing. Therefore, to improve the strength or to have a better control in fabrication, it would be helpful to have a thorough understanding of the diffusions of solvents in polyimide films.

Diffusions of solvents in polyimide films have been studied for a few years.[11–13] However, only the semiflexible polyimide PMDA–ODA (pyromellitic dianhydride–4,4′-oxydianiline) has been investigated, and the results concerning the diffusion mechanism of NMP (*N*-methylpyrrolidinone) seem contradicting. To clarify, the diffusion of NMP in the film of PMDA–ODA is examined in this study. Besides, a rigid rodlike polyimide (PMDA–PDA) is also included to investigate the effect of imide chain structure. Furthermore, the diffusion has been performed in the imide films with different thicknesses and curing temperatures to investigate the effects of film orientation and imidization. To determine the diffusion mechanisms and rates, a bending beam apparatus is used according to the following models.

Theoretical Background

Case I Diffusion Model for Bending Beam Experiment. In the event of case I diffusion, the bending curvature variation of a given bilayer structure composing a polymer overcoat caused by solvent penetration-induced swelling can be correlated to the diffusion coefficient, D, and diffusion time, t, as revealed in the papers by Berry et al.[14] and Jou et al.[15] To generate an entire theoretical curve regarding solvent diffusion-induced curvature variation using the formula presented therein, it requires a complicated numerical computation. However, according to the latter paper, within a relatively short period of diffusion time, the formula for the bending curvature variation ratio, Ω, can be simplified as follow:[15]

$$\Omega = 2(1 + K/2)(Dt/d_f^2)^{1/2}\pi^{-1/2} \tag{1}$$

where Ω is defined as $(1/R_t - 1/R_i)/(1/R_f - 1/R_i)$. R_i, R_t, and R_f are the curvature radii of the specimen as prepared, at any diffusion time, t, and at equilibrium, respectively. d_f and d_1 are the thicknesses of the polymer coating and substrate. K is a function of the ratios of thickness and biaxial modulus of film to substrate, and is defined as follows:

$$K = \frac{2}{(1 + d_1/d_f)}(1 + (d_f/d_1)(E_f^*/E_1^*))$$

where E^* denotes the biaxial modulus.

Equation 1 is a good approximation for $t = 0.54d_f^2/D$ or $\Omega = 0.82(1 + K/2)$.[15] Within the range, a maximum 5% deviation from the exact solution results and the curve of Ω vs $t^{1/2}$ is linear. For $t > 0.54d_f^2/D$ or $\Omega > 0.82(1 + K/2)$, the curve of Ω vs $t^{1/2}$ deviates from linear gradually with the increase of time or Ω.

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In most cases, the tensile modulus of a deposited polymer film is much smaller than that of the substrate, such as silicon or quartz. If the thickness of the polymer film is smaller than the substrate, the term with the biaxial modulus can be ignored and $K \approx 2d_f/(d_f + d_1)$.

By knowing the curvature variation ratios at various times in the initial diffusion stage, one can readily calculate the diffusion constant, D, according to eq 1. On the other hand, if experimental data of Ω vs $t^{1/2}$ exhibit a linear relationship in the initial diffusion stage, the diffusion may belong to case I. Furthermore, if the studied polymer film is so thin that K $(=d_f/d_1)$ is much smaller than unity, the expression in eq (1) can be further simplified and will become the same as that for the weight gain experiment.

Case II Diffusion Model for Bending Beam Experiment. For case II diffusion, the bending curvature variation caused by solvent penetration-induced swelling can be correlated to the diffusion front velocity, v, and diffusion time, t, as revealed in another paper.[16] For thin polymer coating, the bending curvature variation ratio can be simplified as follows:[16]

$$\Omega = vt/d_f \tag{2}$$

There should exist a linear relationship between Ω and t over the entire diffusion process for a given solvent penetrating in a thin polymer film coated on a thick substrate in the event of case II diffusion. By plotting experimental data of Ω against t, one can readily calculate the diffusion front velocity from the slope of the resulting straight line by knowing the film thickness.

With the increase of film thickness, Ω vs t deviates from linear gradually. However, for d_f/d_1 up to 0.05, for example, the linear relationship almost remains unvaried and only a maximum of 5% overestimation results. In this work, all the samples studied have a d_f/d_1 much less than 0.05.

Experimental Section

A. Materials. The starting materials used in this study were dianhydride[17] pyromellitic dianhydride (PMDA) and diamines 4,4′-oxydianiline (ODA), and *p*-phenylenediamine (PDA). The solvent used is *N*-methylpyrrolidone (NMP). These materials were used as received.

B. Polycondensation of Poly(amic acids). PMDA–ODA and PMDA–PDA poly(amic acids) were prepared as follows: In a four-neck round-bottom flask, diamine (ODA or PDA) was dissolved in the NMP solvent. When the diamine had been completely dissolved, equal molar dianhydride (PMDA) was added gradually. The reaction proceeded for 5 h with stirring. The entire process was done under nitrogen atmosphere, and the temperature was kept at 40 °C. The resulting solution had a solid content of 14 wt %.

C. Bending Beam Specimen Preparation. The substrates used for bending curvature measurements were silicon strips with a 7.0-cm length, 0.8-cm width, and 370-μm thickness. These silicon strips were prepared by slicing (100) silicon wafers along the (100) crystal plane. Polyimide films were prepared by spin-casting their poly(amic acid) solutions on the substrates. This was followed by prebaking at 80 °C for 30 min, and then curing to 200, 250, 300, 350, or 400 °C with a ramp rate of 2 °C/min. Since one end of the substrate must be mounted on a clamp and the other end must reflect laser beam to a sensor, the two ends of the solid film were removed by 1 cm.

D. Bending Curvature Measurements. The schematic diagram of the bending curvature measurement using a bending beam apparatus is described in ref 16. Before being measured, the samples were kept in a vacuum chamber to prevent moisture uptake. To measure its bending curvature by using the bending beam apparatus, the specimen was mounted on a clamp and then immersed in a sample cell containing NMP solvent. The deflection of the free end of the specimen was measured continuously during solvent diffusion. According to the geometry of the setup, the obtained position data were then converted to bending curvature. The entire diffusion experiments were performed at ambient temperature.

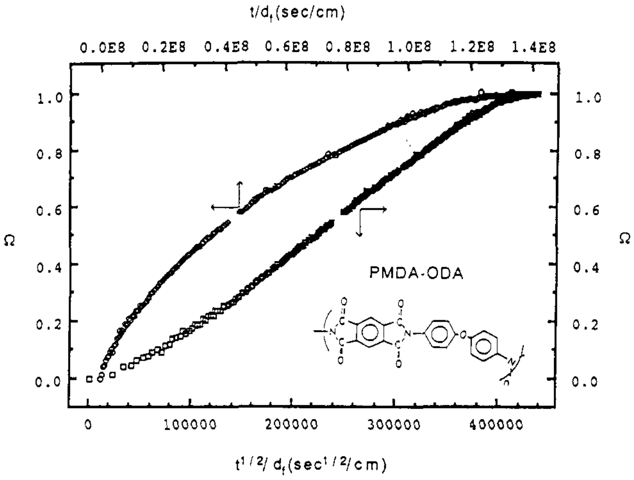

Figure 1. Measured bending curvature variation ratio, Ω, vs diffusion time for the diffusion of NMP solvent at room temperature in the imide film of PMDA–ODA, which has been cured to 350 °C and has a thickness of 7.3 μm. The curve of Ω vs $t^{1/2}$ is linear, indicating a case I diffusion.

E. X-ray Diffraction Specimen Preparation. To investigate the effect of the absorbed solvent on the morphology of the imide film of PMDA–PDA, an out-of-plane X-ray diffraction experiment was performed. The X-ray specimen was prepared by stacking together many layers of the PMDA–PDA films prepared similarly as mentioned above. The resulting specimen was thicker than 200 μm so that the applied X-ray would not penetrate through the films and one could then compare the results quantitatively. X-ray diffraction patterns were taken for the dried specimen, as prepared, and after fully swollen.

F. X-ray Diffraction Experiment. The X-ray diffraction experiment was done by using a Rigaku wide-angle X-ray diffractometer with a nickel-filtered Cu Kα1 radiation. Its power was set at 40 kV and 20 mA. The arrangements of the X-ray diffraction experiment are described in ref 17.

Results and Discussion

Diffusion in PMDA–ODA. The diffusion of NMP solvent in the film of PMDA–ODA coated on a silicon substrate measured by the usage of a bending beam apparatus is shown in Figure 1. Except in the very beginning, the resulting bending curvature variation ratio, Ω, vs $t^{1/2}$ exhibits a linear relationship for $\Omega < 0.8$, indicating a case I diffusion. By plotting Ω against t, no linear relationship could be observed, clearly indicating not a case II diffusion. The deviation from linearity in the beginning may be attributed to an induction behavior. Here, the film has been cured to 350 °C and has a thickness of 7.3 μm.

As known, PMDA–ODA film structure is relatively amorphous according to an X-ray diffraction study.[17] For amorphous polymers, "voids" could easily form among chains or chain segments. If the voids are large enough, they would allow NMP molecules to penetrate more freely, and this would result in a case I diffusion. Actually, case I behavior has been observed in the diffusion of NMP in another amorphous polyimide film, composed of 6FDA–PDA (6F dianhydride–phenylenediamine), in a previous study.[16] Due to the fact that the film of 6FDA–PDA would dissolve in NMP if being cured at temperatures below 350 °C, it is not suitable for this study.

Similar studies have been performed by Gattiglia et al.[11] and Tong et al.[12] The diffusion of NMP in PMDA–ODA films has been reported to belong to case II by the former group, while an anomalous but close to case I

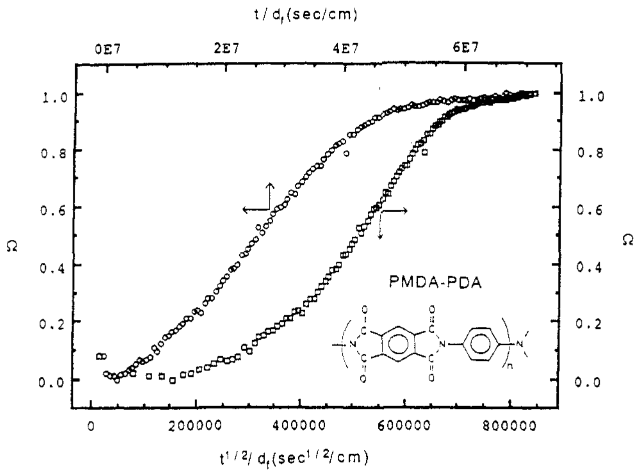

Figure 2. Measured bending curvature variation ratio, Ω, vs diffusion time for the diffusion of NMP solvent at room temperature in the imide film of PMDA–PDA, which has been cured to 350 °C and has a thickness of 1.0 μm. The curve of Ω vs t is linear, indicating a case II diffusion.

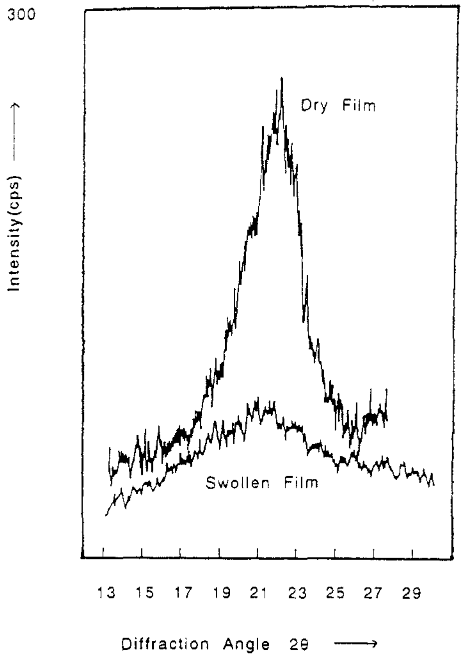

Figure 3. Variation of the out-of-plane X-ray diffraction pattern of the film of PMDA–PDA upon absorbing NMP solvent.

diffusion behavior has been declared by the latter group. By carefully examining the diffusion data presented in ref 11, the weight gain data vs t is not a straight line, but curvelike. It would be more like a straight line if the data were replotted against $t^{1/2}$. By so doing, one also would not observe a "negative induction time" as reported in the literature.[11] This indicates that the diffusion of NMP in PMDA–ODA should not be case II. As to the latter study,[12] the data points presented do not seem to make any conclusive remark.

Diffusion in PMDA–PDA. The diffusion of NMP solvent in the film of PMDA–PDA is shown in Figure 2. Contrary to PMDA–ODA, the resulting bending curvature variation ratio, Ω, vs $t^{1/2}$ for PMDA–PDA is obviously not linear, but linear for Ω vs. t. This indicates that the diffusion of NMP in PMDA–PDA film belongs to case II. Here, the film has been cured to 350 °C and has a thickness of 1.0 μm.

Unlike PMDA–ODA, the PMDA–PDA film structure is highly crystalline, as demonstrated in Figure 3. In highly crystalline polymers, large voids could hardly form among chains or chain segments within crystallites. For NMP molecule diffusion to proceed, large voids must be created. This requires the imide chains or chain segments in the crystallites to relax first. Unlike in an amorphous polymer, the relaxation of the chains in a crystalline polymer would be more time-consuming. As a result, this chain relaxation would become a diffusion-limiting step and result in a case II diffusion.

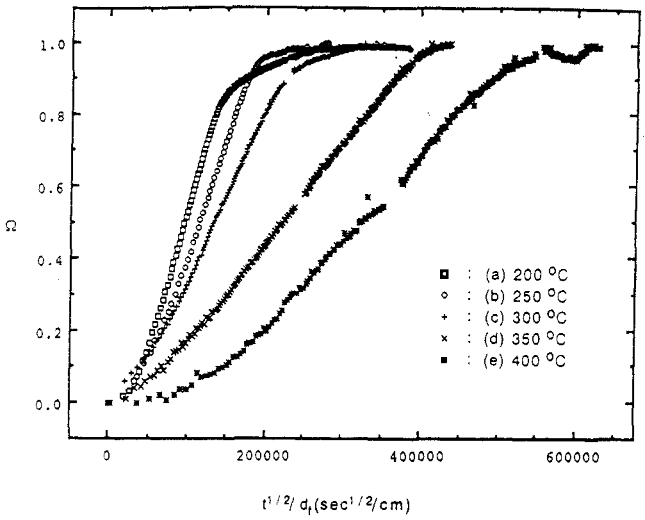

Figure 4. Effect of curing temperature on the diffusion of NMP in the films of PMDA–ODA. For curing temperatures of (a) 200, (b) 250, (c) 300, (d) 350, and (e) 400 °C, the calculated diffusion coefficients are 4.8, 3.3, 1.8, 0.60, and 0.46 × 10^{-11} cm^2/s, respectively.

Typically, crystalline polymers are very difficult to dissolve or swell at temperatures well below their melting points, even in good solvents. However, NMP can penetrate and has, actually, penetrated into the crystallites and destructed some ordering of the PMDA–PDA film, as evidenced in Figure 3. The diffraction peak of PMDA–PDA, which results from the intermolecular ordering of the imide chains, dropped significantly upon absorbing NMP. Furthermore, the ordering has not been completely destroyed, indicating the likelihood of the existence of cross-links in the film.

Curing Effect. In the above experiments, the films have been cured to 350 °C. The effect of the curing temperature on the diffusion of NMP in the films of PMDA–ODA is shown in Figure 4. Regardless of curing temperature, all these diffusions belong to case I. The diffusion process obviously becomes slower with the increase of the curing temperature. For curing temperatures of 200, 250, 300, 350, and 400 °C, the calculated diffusion coefficients are 4.8, 3.3, 1.8, 0.60, and 0.46 × 10^{-11} cm^2/s, respectively.

PMDA–ODA films would imidize more completely with the increase of the curing temperature from 200 to 400 °C.[17] Upon imidization, the chain structure would convert from a relatively flexible amic acid to a less flexible imide. The reduction in the chain irregularity could lead to a better packing and result in a reduction of voids and/or void size. As a result, the diffusion coefficients of NMP in these PMDA–ODA films decrease with the increase of the curing temperature.

The effect of the curing temperature on the diffusion of NMP in the films of PMDA–PDA is shown in Figure 5. Regardless of curing temperature, all these diffusions belong to case II. Similarly, the diffusion process becomes slower with the increase of the curing temperature. For curing temperatures of 200, 250, 300, 350, and 400 °C, the calculated diffusion front velocities are 1.0, 0.70, 0.34, 0.23, and 0.099 × 10^{-7} cm^2/s, respectively.

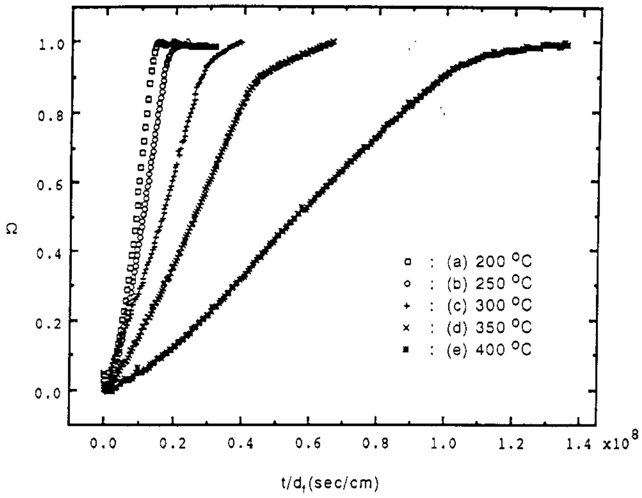

Figure 5. Effect of curing temperature on the diffusion of NMP in the films of PMDA–PDA. For curing temperatures of (a) 200, (b) 250, (c) 300, (d) 350, and (e) 400 °C, the calculated diffusion front velocities are 1.0, 0.70, 0.34, 0.23, and 0.099 × 10^{-7} cm^2/s, respectively.

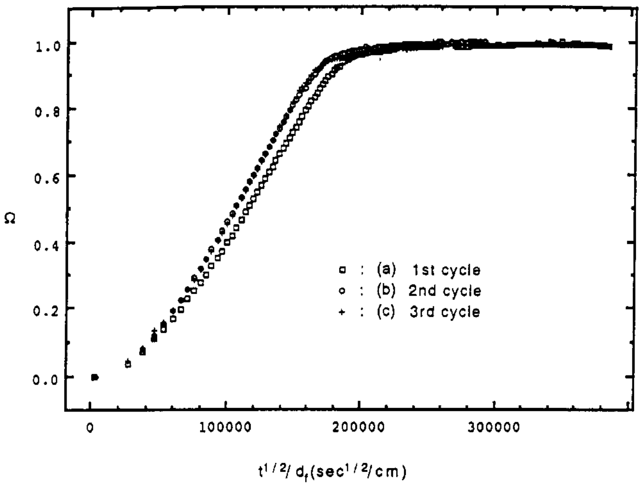

Figure 6. Effect of diffusion history on the diffusion of NMP in one PMDA–ODA film cured at 250 °C. The diffusion coefficients are 3.3, 3.8, and 3.9 × 10^{-11} cm^2/s, respectively, for the film (a) when newly prepared and (b) after one and (c) two diffusion/drying cycles.

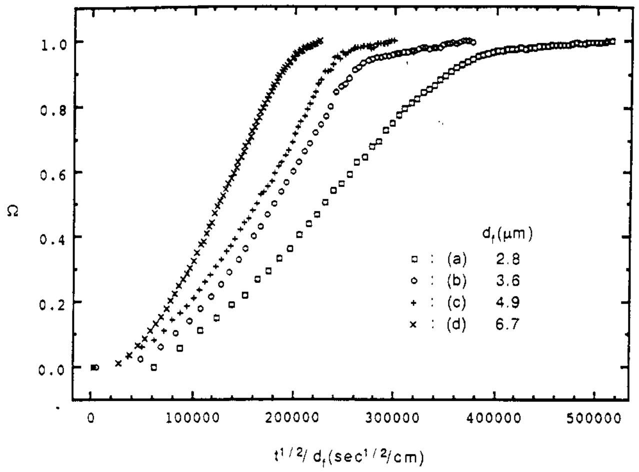

Figure 7. Effect of film thickness on the diffusion of NMP in the film of PMDA–ODA cured at 250 °C. The calculated diffusion coefficient increases from 3.7 to 6.9 × 10^{-11} cm^2/s for thickness increasing from 2.8 to 6.7 μm.

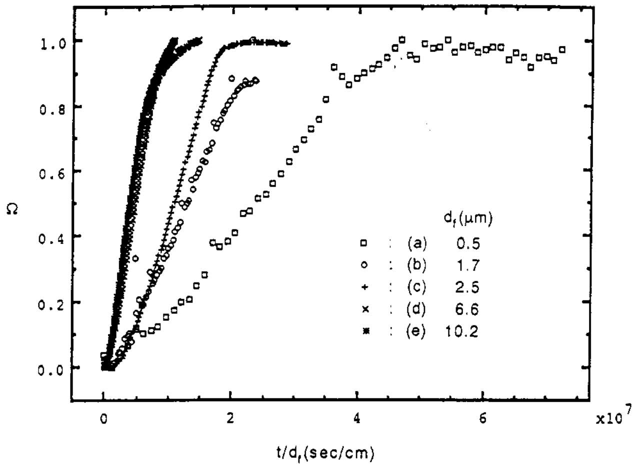

Figure 8. Effect of film thickness on the diffusion of NMP in the film of PMDA–PDA cured at 250 °C. The calculated diffusion front velocity increases from 2.6 to 14.4 × 10^{-8} cm/s for thickness increasing from 0.5 to 10.2 μm.

Effect of Diffusion History. The effect of diffusion history on the diffusion of NMP in one PMDA–ODA film cured at 250 °C has been investigated. As seen in Figure 6, its case I diffusion behavior remains unchanged when subjected to a repeated diffusion/drying process. As calculated, the diffusion coefficients are 3.3, 3.8, and 3.9 × 10^{-11} cm^2/s, respectively, for the film when newly prepared, after one and two diffusion/drying cycles. The diffusion coefficient increased slightly the second time and became unchanged thereafter. This clearly indicates that the diffusion process is reversible. The film morphology must not have been altered by the prior absorbed solvent after drying. Since the film could absorb, at least, from 10% to 100% by weight of NMP, depending on the film thickness, and swell likewise in the film transverse direction, the reversible phenomenon indicates that the film has at least some degree of cross-linking. Otherwise, the film of PMDA–ODA might have been dissolved and the film integrity might have been destroyed, and as a result, the diffusion process would not be reversible.

Effect of Film Thickness on Diffusion. The effect of film thickness on the diffusion of NMP in the film of PMDA–ODA cured at 250 °C is shown in Figure 7. All the diffusion processes begin with a nonlinear "induction region" and then proceed linearly. By comparing the curves of Ω vs. $t^{1/2}$ with those of Ω vs t, it can be clearly found that Ω vs t is not linear throughout the entire diffusion process. Furthermore, if the data were plotted against t, a negative induction time would have been obtained. These obviously indicate that the diffusion should not be case II. On the contrary, a linear relationship can be observed when plotting the data against $t^{1/2}$, though some of the diffusion curves seen to have a much longer induction period. However, they become linear at a slightly higher Ω value. Therefore, these diffusion processes should be case I. The diffusion process becomes faster when the film thickness increases. The calculated diffusion coefficient increases from 1.2 to 3.7 × 10^{-11} cm^2/s for thickness increasing from 2.8 to 6.7 μm. Such a trend is in accordance with that reported by Gattiglia et al.[11]

The effect of film thickness on the diffusion of NMP in the film of PMDA–PDA cured at 250 °C is shown in Figure 8. All the diffusion processes exhibit unanimously a case II mechanism. The diffusion process becomes markedly faster when the film thickness increases. The calculated diffusion front velocity increases from 2.6 to 14 × 10^{-8} cm/s for thickness increasing from 0.5 to 10.2 μm.

The increases in the diffusion coefficient and diffusion front velocity with respect to thickness may be attributed to the fact that the film orientation and/or ordering decrease with the increase of film thickness, as revealed

Table I
Dependences of Weight Gain and Diffusion Coefficient on Film Thickness for the Films of PMDA-ODA Cured at 250 °C

film thickness (μm)	2.8	3.6	4.9	6.7
D ($\times 10^{11}$ cm^2/s)	1.2	2.2	2.1	3.7
weight gain ((g/g of PI) × 100)[a]	101	65	65	51

[a] PI denotes polyimide.

Table II
Dependences of Weight Gain and Diffusion Front Velocity on Film Thickness for the Films of PMDA-PDA Cured at 250 °C

film thickness (μm)	0.5	1.7	2.5	6.6	10.2
v ($\times 10^8$ cm/s)	2.6	4.8	6.9	12.9	14.4
weight gain ((g/g of PI) × 100)[a]	286	93	71	32	32

[a] PI denotes polyimide.

in a previous study using X-ray and FTIR.[17] As known, it is more difficult for solvent molecules to penetrate into a film with a higher degree of film orientation or ordering, and vice versa.

Effect of Film Thickness on Weight Gain. For the same PMDA-ODA films mentioned above, their weight gains upon absorbing NMP are shown in Table I. Contrary to the diffusion result, the weight gain decreases when the film thickness increases. It decreases from 101 to 51 wt % for thickness increasing from 2.8 to 6.7 μm. In Gattiglia et al.'s study,[11] the weight gain decreases from 30 to 10 wt % for thickness increasing from 10 to 60 μm. The decreasing weight gain tendency with respect to thickness observed in our study is in accordance with their result. Beside the consistency in the trends observed, it is also very interesting to see that the absolute magnitudes of the weight gains measured by two different groups are in fairly good agreement, that is, that one may obtain a weight gain result similar to theirs by extrapolating our data to the higher thickness range, and vice versa. However, it is noteworthy that their films were cured at 300 °C, and ours at 250 °C.

For PMDA-PDA films, the weight gains upon absorbing NMP are shown in Table II. Similar to the trend observed in PMDA-ODA, the weight gain decreases when the film thickness increases. It decreases from 286 to 32 wt % for thickness increasing from 0.5 to 10.2 μm.

The above phenomenon may be related to the film cross-linkability. As known, unlike on-substrate-cured, a freely cured PMDA-ODA film does not exhibit any film orientation and would hardly absorb NMP or swell. If it has been stretched to some extents, such as 1.5 or 2 times its original length, it would then absorb a great deal of NMP and swell markedly. No absorption or swelling phenomenon could be observed if the stretching extent was not high enough. It seems very likely that a freely cured film, which exhibits no film orientation and solvent absorption or swelling, must be highly cross-linked. The cross-linking should originate from the formation of intermolecular links (called transimides) in the imide film upon curing, as reported in several studies.[17-19] The links, like the links in many other networking polymers, would not be broken unless being stretched to a certain level. Furthermore, if the freely cured film were lightly cross-linked, it should have been able to swell more or less when being immersed in NMP without the help of stretching. Therefore, the film must be highly cross-linked. This may be used to explain why there exists an abrupt change in swelling or solvent uptake in the freely cured film.

The on-substrate-cured films studied here have been biaxially stretched or oriented upon curing. Such an inherent stretching effect may result in the scission of some of the intermolecular links or in deed hinder the formation of some intermolecular links during curing. This would result in a film with a less degree of cross-linking and then make the absorption of NMP in these films possible. The degrees of cross-linking or the densities of the intermolecular links in these on-substrate-cured films must be much lower than that in the freely cured film so that these films could absorb a significant amount of NMP as observed.

From the above results, it can be seen that the formation of cross-links or intermolecular links seems to be unfavored in an oriented or stretched film. As mentioned previously, thicker films that cured on substrates would have a poor film orientation. This also means that thicker films would be stretched less, on average, upon curing. Therefore, a higher degree of cross-linking or a higher density of intermolecular links could be expected to form in the thicker films. As known, a polymer with a higher degree of cross-linking would absorb much less solvent or be more difficult to swell. This may be used to explain why the weight gains in both the films of PMDA-ODA and PMDA-PDA decrease with the increase of film thickness.

Conclusion

From this study, it may be concluded that the diffusion of NMP solvent in PMDA-ODA imide films belongs to case I diffusion, while that in PMDA-PDA belongs to case II. The difference may presumably be attributed to the fact that PMDA-ODA is relatively flexible and can form an amorphous and large void-rich film structure so that NMP molecules can penetrate more freely, while PMDA-PDA is rigid and can form a highly crystalline and large void-free film structure so that NMP molecules need to relax the chains first in order for diffusion to proceed. The diffusion mechanisms do not vary with thickness ranging from 0.5 to 10 μm or curing temperature from 200 to 400 °C, while the diffusion processes apparently become faster with the increase of the thickness and decrease of the curing temperature. The latter phenomena can be correlated to the film ordering and/or orientation that decrease with the increase of the film thickness and decrease of the curing temperature. The reversibility in the diffusion process upon repeated diffusion/drying cycles indicates that the films studied must be cross-linked. The decreasing trend in solvent weight gain with respect to thickness in both polyimides implies that the degree of cross-linking in these on-substrate-cured films increases with the increase of the film thickness.

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Registry No. PMDA–ODA (copolymer), 25038-81-7; PMDA–ODA (SRU), 25036-53-7; PMDA–PDA (copolymer), 25038-82-8; PMDA–PDA (SRU), 26099-65-0; NMP, 872-50-4.