

Dynamics of Solvent Diffusion in an Aromatic Polyimide

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SYNOPSIS

Diffusion behaviors of two polyimides (PIs) synthesized from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydianiline (ODA), and 4,4'-diaminodiphenylsulfone (DDS) were investigated by the gravimetric method. The weight uptake of penetrants (solvents) was nearly proportional to the exposure time in solvent. This phenomenon was considered as the Case II diffusion (non-Fickian) mechanism. Two PI films had an affinity to *N*-methyl-2-pyrrolidinone (NMP) rather than to dimethylsulfoxide (DMSO). The solubility parameter differences between two polyimides and NMP are less than 5, whereas that between polyimides and DMSO are greater than 5, as calculated by Hoy's group contribution method. The solvent uptake of anisotropic films contributed to an increase in the thickness. The swollen amount of anisotropic films increased with the swelling temperature but tended to decrease with the imide content and the thickness of the anisotropic films. Isotropic films of two PIs did not swell in both NMP and DMSO. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Recently, much demand has been continued for the high heat-resistant and high-performance polymers in the fields of the electronic and aeronautical industry since the last three decades. Particularly, the development and application of electronic materials are very important to photo- and electron-beam resists, printed circuit boards, fabrication of semiconductor devices, interlayer insulators, and information storage media. In the application to chip device techniques, the aromatic polyimide is used as dielectric insulators and photoresists due to its excellent mechanical, thermal, and dimensional stability.¹⁻³ Especially, thin polyimide films prepared via the solvent-cast method followed by thermal cyclimidization have a process that involves the exposure in stripping fluids (solvents or penetrants used in microprocessing). Therefore, in new microelectronic techniques for the development of chip fabrication, it is very essential to consider the diffusion relationship between polyimide films and all of the penetrants.

Permeability of polymers results from change of physical and chemical factors of polymer and penetrant and thus causes the polymer molecular motion and creep phenomenon. Day⁴ studied the effect of moisture in polyimide (PI) film from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) on the performance for microdielectric sensors, and the diffusion coefficient based on Fick's law was calculated. The sorption and transport of water and ammonia in pyromellitic dianhydride (PMDA)/ODA PI film (DuPont, Kapton type) were also investigated by Iler et al.⁵ and this swelling behavior obeyed Fickian behavior as well.

In recent years, many publications about Case II diffusion, originally discussed by Alfrey,⁶ have appeared. Diffusional aspects of Case II diffusion differ from Fickian behaviors, leading to time-independent and constant diffusion coefficients. Furthermore, the weight gain of sorbed polymer obeyed linear kinetics with exposure time in sorbents, e.g., Thomas and Windle's study^{7,8} of the poly(methyl methacrylate) (PMMA)/methanol system. Particularly, sharp moving boundaries followed by a retardation process were detected by birefringence measurement^{8,9} and a microscopy technique.⁹ Imaging techniques¹⁰ using the nuclear magnetic resonance (NMR) method

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were also successively employed to show that the advance of the sharp concentration front was linear with the time of the PMMA sphere and methanol system. In Case II diffusion, the diffusion coefficient can be a variable and must also be dependent on diffusion history and have the sharp fronts with constant velocity simultaneously.

Tong and Saenger¹¹ analyzed the diffusion behaviors of PMDA/ODA PI, DMSO, and NMP and classified them as pseudo-Fickian transport, Case II diffusion, and intermediate transport using laser interferometry. Gattiliglia and Russell¹² also studied the diffusion behaviors of Kapton/NMP or DMSO and considered this phenomenon as the Case II diffusion mechanism different from the swelling system of PI and water and ammonia. They reported that DMSO could swell PMDA/ODA PI film more rapidly than could NMP at temperatures ranging from 20 to 150°C, mainly due to the smaller molecular volume of DMSO (71.3 cm³/mol) in comparison to NMP (96.6 cm³/mol) and variance in the interaction parameter of PI/solvents.

The objective of this study was to investigate the effect of swelling temperature, penetrants (NMP and DMSO), film thickness, manufacturing conditions (orientation or ordering), and imide content of BTDA-type PI films on the diffusion behaviors and to compare the phenomenological diffusion aspects with Kapton PI film.

EXPERIMENTAL

Reagents

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Aldrich Chemical Co. and recrystallized from acetic anhydride followed by drying at 170°C for 28 h under vacuum prior to use. 4,4'-Oxydianiline (ODA) and 4,4'-diaminodiphenylsulfone (DDS) from Aldrich Chemical Co. were recrystallized from ethanol. *N*-Methyl-2-pyrrolidinone (NMP, Aldrich Chemical Co.) as the reaction solvent was dehydrated with calcium hydride (Junsei Chemical Co., Japan) and distilled under reduced pressure. NMP (HPLC grade, Aldrich Chemical Co.) and DMSO (99.9%, Junsei Chemical Co.) were used as swelling agents without further purification.

Preparation of Polyamic Acid (PAA) and Polyimide (PI)

To prepare polyamic acid (PAA), 14.42 g (0.072 mol) of ODA (or DDS) was dissolved in 142 mL of

NMP at room temperature and added with 22.56 g (0.07 mol) of BTDA and 61 mL of NMP to wash BTDA slurry remaining inside the flask. The polymerization reaction was carried out at room temperature for 1 day to obtain homogeneous PAA according to the general methods described elsewhere.^{13,14} The resulting solutions of PAA were precipitated repeatedly in acetone and methanol, respectively, filtered, and dried at 70°C for 1 day.

Dried yellow PAA powder was dissolved in NMP to make a 15–20 wt % solution, followed by casting on a glass plate, and then was thermally cured stepwise in a static air oven according to the conditions listed in Table I. Imide contents (partially imidized PIs and fully cured PIs) were calculated from the difference of weight losses from 80 to 400°C after thermogravimetric analysis.^{15,16}

Swelling Test

Swelling experiments in this research were carried out by immersion of 10 × 50 mm bar-type PI films. The solvent uptake (W/W_0 , where W_0 = initial weight of nonswollen film and W = cumulative weight of swollen film at any time) of swollen PI films was measured on a gravimetric balance after exposing the PI films in solvent and wiping the film surface cautiously with Kimwipes paper tissues. The same PI specimen measured was returned to the solvent for later swelling tests. The swelling temperature in this study was measured by the blank test tube equipped with thermometer in a silicone oil bath.¹²

Although the gravimetric measurement is very simple and general, this method often gives rise to inappropriation of swelling experiments if the solvent penetrates very rapidly into the diffusion media, i.e., sheet or film. More accurate procedures for swelling kinetics were used to obtain profiles of penetrant diffusing into glassy polystyrene by Rutherford backscattering spectrometry.^{17–19} Laser interferometry¹¹ was employed to study the diffusion into PI film coated on a substrate. NMR imaging techniques were also suited for investigating dynamic systems of the diffusion into polymers.¹⁰

Characterization

Chemical structures of PAA were confirmed by using FTIR (Nicolet, Model 5DX). Inherent viscosity (η_{inh} , dL/g) was measured at 25°C with NMP (0.5 wt %), using an Ubbelohde viscometer. Glass transition temperatures of cured polyimide were detected using a differential scanning calorimeter (DSC,

Table I Curing Conditions of Anisotropically Oriented Polyimide Films

| Monomer System | Sample Designation | Thermal Treatment | Imide Content (%) ^a |
|----------------|--------------------|--|--------------------------------|
| BTDA/DDS | BD-25 | 100°C, 1 h/200°C, 1 h | 25 |
| | BD-70 | 100°C, 1 h/200°C, 1 h 300°C, 1 h | 70 |
| | BD-100 | 100°C, 1 h/200°C, 1 h 300°C, 1 h/350°C, 1 h | 100 |
| BTDA/ODA | BO-71 | 155°C, 3 h/200°C, 1 h | 71 |
| | BO-85 | 100°C, 1 h/200°C, 1 h 300°C, 1 h | 85 |
| | BO-87 | 155°C, 3 h/200°C, 1 h 250°C, 1 h | 87 |
| | BO-96 | 155°C, 3 h/200°C, 1 h 300°C, 1 h | 96 |
| | BO-100 | 155°C, 3 h/200°C, 1 h 300°C, 1 h/350°C, 1 h | 100 |

^a See Refs. 15 and 16.

DuPont Model 910) attached to 2100 thermal analyzer computer system at a programmed heating rate of 20°C/min under nitrogen (50 mL/min). Thermogravimetric analysis (TGA, DuPont Model 951) was conducted from 40 to 1000°C at a programmed heating rate of 20°C/min under a nitrogen atmosphere. The gravimetric balance (Mettler, Model AE 163) was used to measure the weight uptake of penetrants and had a capability of accuracy to ± 0.1 mg.

The thickness and lateral dimensions during swelling tests were measured by a thickness dial gauge (Ozaki, Japan, Model G, 0.01×10 mm) and computerized micrometer (Brown & Sharpe Digit-Cal., Plus, USA, Model 599-571-3), respectively.

RESULTS AND DISCUSSION

FTIR spectra for PAA from BTDA/ODA showed the characteristic absorption bands^{14,15} at 1660 cm^{-1} (amide I) and 1545 cm^{-1} (amide II) (not shown here). The characteristic peaks for PI appeared at 1778 , 1720 , 1380 , and 725 cm^{-1} and the intensity of these peaks increased during imidization at high temperature. Disappearance of a peak at 1545 cm^{-1} (amide II) indicated the conversion of PAA into PI due to the formation of imide ring after thermal cyclimidization.^{13,14,16,20,21}

There were several reports on the calculation of the relative degree of imidization using FTIR,²²⁻²⁶ TGA,^{15,16} and the optical density technique.²⁷ In this study, we employed the TGA method that was sug-

gested by Omote et al.¹⁵ Thus, imide contents (%) were calculated from the equation $(W_U - W_T)/W_U \times 100$, where W_U and W_T are the percent weight loss for cyclization of uncured and cured films at any imidization temperature T (°C), respectively. Therefore, the value (imide content) of $(W_U - W_T)/W_U \times 100$ increased when imidization was carried out at a higher temperature and longer time.

Figure 1 shows TGA thermograms of PIs from BTDA/ODA and BTDA/DDS. BTDA/ODA PI was more heat-resistant than was BTDA/DDS PI. Table II summarizes inherent viscosities of PAAs and thermal properties of fully cured PIs.

Ikeda²⁸ and Russell et al.²⁹ reported that the cured PI film on the substrate exhibited a significant orientation of molecules parallel to the surface of the film. The morphology of isotropic PMDA/ODA PI was studied using small-angle X-ray scattering.³⁰ Wide-angle X-ray diffraction by Yoon et al.³¹ was also used to investigate the molecular order of oriented and unoriented PMDA/ODA PI film.

Orientation of polymeric materials introduces an asymmetric structure such that diffusion rates vary relative to the axis of orientation. Generally, it is known that the diffusion rate of penetrants parallel to the axis is less than the rate perpendicular to the axis in a randomly oriented swelling body.³²

The validity of this generalization was applied to the BTDA/DDS or ODA PI system. PI films imidized on a substrate exhibit in-plane orientation of macromolecular chains, which is called an anisotropic ordering, and can easily swell in solvents.^{9-12,32} However, solvents or diffusants do not permeate into

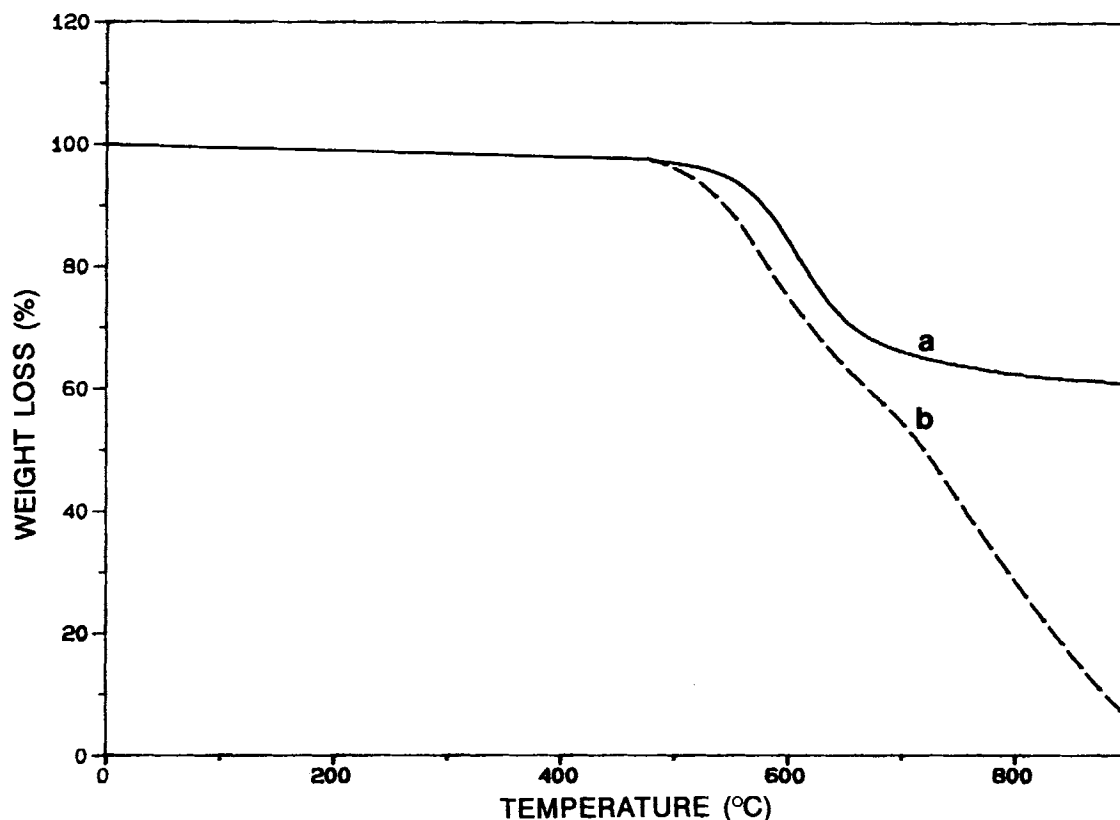


Figure 1 TGA thermograms of PI from (a) BTDA/ODA (—) and (b) BTDA/DDS (---); heating rate = 20°C/min.

the isotropic films imidized in a free-standing or no-substrate state. In the case of anisotropic BTDA/DDS polyimides (BD-70 and BD-100), the weight uptake (W/W_0) of swollen anisotropic BD-70 and BD-100 films after the exposure in NMP and DMSO decreased with the increase of imide ring formation [see Fig. 2(a) and (b)]. The affinity of PI to NMP was stronger than that of PI to DMSO for both BD-70 and BD-100 films. Fully cured BTDA/DDS PI film is insoluble at room temperature in polar solvents such as NMP, DMSO, *N,N*-dimethylacetamide (DMAC), etc. However, when the swelling temperature is raised to 80°C, the swollen amount (W/W_0) of the BD-100 PI film was considerably

increased to about 2.8 and the surface of the BD-100 film appeared to be rough because of molecular relaxation via solvent induction. The BD-100 film cleanly dissolved in NMP after the exposure time of 800 min. Due to the solubility, the swelling test of the BTDA/DDS PI system could not be continued further. In comparison, this diffusion process followed by dissolution undertook very slowly in DMSO and also dissolved after 1200 min.

Figure 3(a) showed the weight uptake of anisotropic BO-96 PI film measured at 80°C. The diffusion behaviors of BTDA-type PI based on linear kinetics have been previously confirmed as the examples of Case II diffusion as in the case of the BD

Table II Inherent Viscosity, Glass Transition Temperature, and Thermal Stabilities of Fully Cured BTDA/DDS PI and BTDA/ODA PI Systems

| Sample | η_{inh} (dL/g) ^a | T_g (°C) | T_{10} (%) | T_{max} (%) |
|--------|----------------------------------|------------|--------------|---------------|
| BD-100 | 0.53 | 256 | 542 | 575 |
| BO-100 | 0.57 | 295 | 571 | 615 |

^a Inherent viscosity of polyamic acid in NMP at room temperature (0.5 wt %).

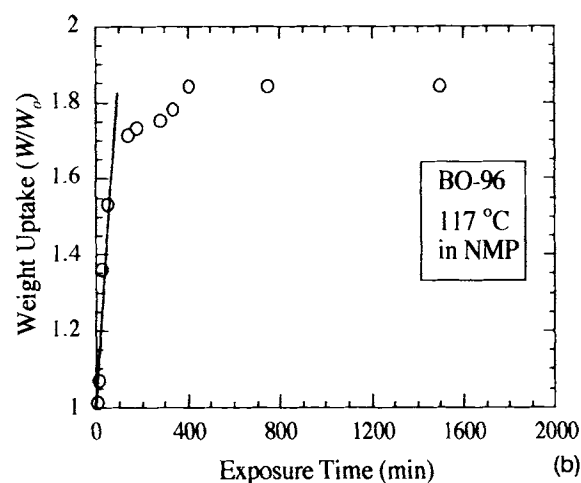
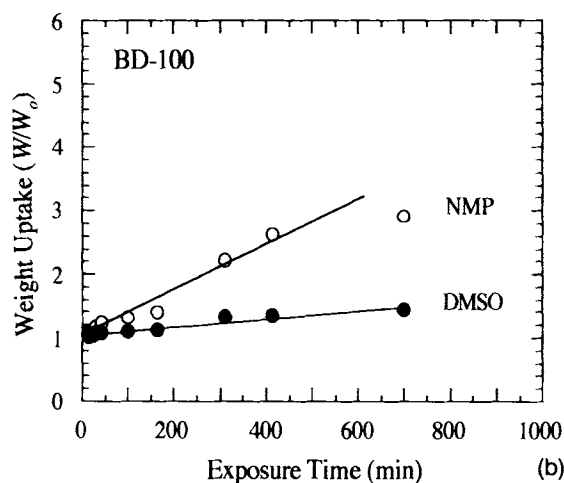
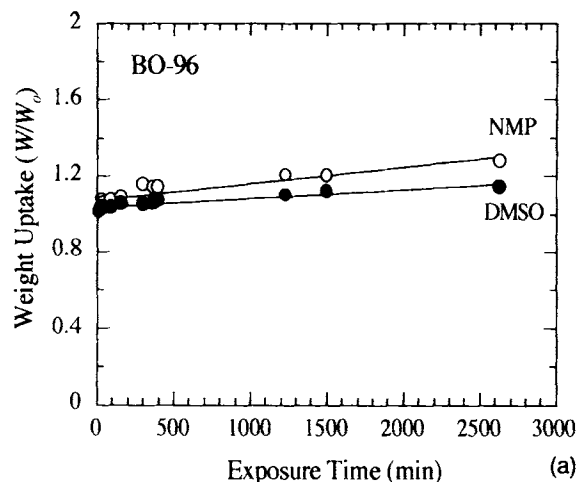
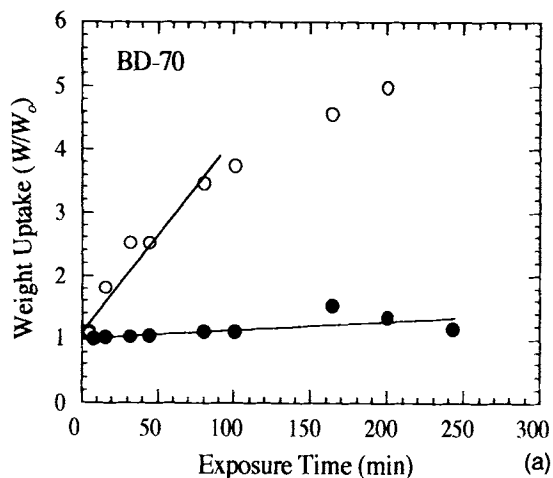


Figure 2 (a) Solvent weight uptake of anisotropic BD-70 cured at 100°C, 1 h/200°C, 1 h/300°C, 1 h, and swollen with (○) NMP and (●) DMSO at 80°C. (b) Solvent weight regain of anisotropic BD-100 cured at 100°C, 1 h/200°C, 1 h/300°C, 1 h/350°C, 1 h and swollen with (○) NMP and (●) DMSO at 80°C.

PI system. This film also exhibited a good affinity to NMP rather than to DMSO. The weight gain (W/W_0) of swollen BO-96 PI film was about 1.28 in NMP and 1.1 in DMSO after swelling for 47 h. Linear kinetic behaviors of weight gain of polymer with time was observed in DMSO as well as in NMP, similar to the study of Alfrey⁶ in the polystyrene/acetone system and studies of Tong and Saenger¹¹ and Gattiliglia and Russell¹² in the Kapton PI/NMP (DMSO) system, respectively.

These results on swelling behavior of anisotropic BTDA-type PI with NMP and DMSO were in contradiction to what Tong and Saenger¹¹ and Gattiliglia and Russell¹² reported on the Kapton and NMP or DMSO. Their analysis was based on the

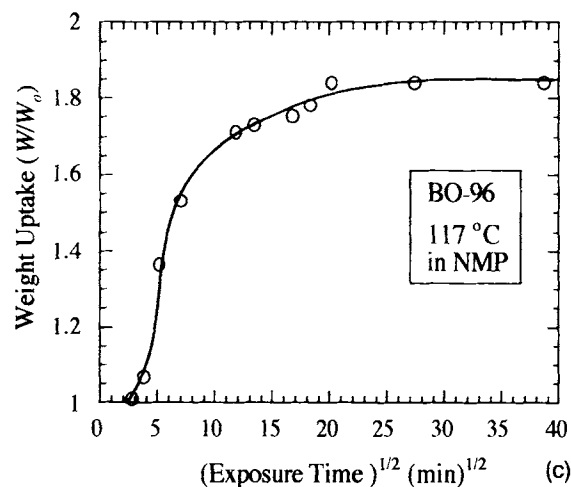


Figure 3 (a) Swelling behaviors of anisotropic BO-96 imidized at 155°C, 3 h/200°C, 1 h/300°C, 1 h, swelling solvent; (○) NMP and (●) DMSO at 80°C. (b) Solvent uptake vs. time of BO-96 PI film measured at 117°C swollen with NMP. (c) Solvent uptake vs. square root of time of BO-96 PI film measured at 117°C.

fact that their PI was more swollen in DMSO than in NMP due to a smaller molar volume of DMSO and the difference in interaction parameters of PI film and solvents but without any detailed analysis or data. From the resulting experimental data of BTDA/DDS and BTDA/ODA systems, carbonyl group in BTDA might have a strong interaction with the amide bond in NMP rather than with the sulfide group in DMSO. Aromatic diamine (ODA or DDS) in the imide backbone may contribute to the interaction with any penetrants, but more direct effects are expected to be the cause of the interaction of BTDA with solvents.

Table III lists the solubility parameters of solvents, BTDA/DDS PAA and BTDA/ODA PAA, calculated from Hoy's method.³³ We used the group contribution methods for calculating solubility parameters of amic acids since assignments of group contribution for the imide ring structure have not been carried out by other physical chemists. For the same reasons, the sulfone group in DDS and sulfide in DMSO were substituted for the sulfide group for convenience's sake because of difficulty in finding two group contributors.

Hoy's method is more logical than that of Hoftyzer and Van Krevelen³³ in that the molecular aggregation number of polymer and solvent, the number of repeating units per effective chain segments of polymer, and base values of polymer and solvent are used for evaluating relationship (or auxiliary equation) between the low molecular weight liquid (solvent) and the amorphous polymer. Our experimental results were based only on Hoy's method because the group contributors for the amide group had not been studied in Hoftyzer and Van Krevelen's method and might distort the calculation of F_{di} , F_{pi} ,

Table III Estimation of Solubility Parameters of BTDA/DDS PAA, BTDA/ODA PAA, and Solvents Calculated from Hoy's Method

| Material | δ^a | δ_d | δ_p | δ_h |
|-------------------|------------|------------|------------|------------|
| NMP | 26.5 | 17.0 | 13.3 | 15.4 |
| DMSO ^b | 21.5 | 14.4 | 10.0 | 12.3 |
| BD ^c | 25.5 | 15.8 | 15.1 | 13.2 |
| BO | 25.8 | 16.0 | 15.0 | 13.5 |

^a $\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$, where δ_d , δ_p , and δ_h mean factor of dispersion force, polar force, and hydrogen bonding, respectively, and each solubility component was evaluated using additive molar functions, auxiliary equations, and group contributors (see Ref. 33).

^{b,c} Sulfone group (O=S=O) in DDS and sulfoxide group (>S=O) in DMSO were replaced with the sulfide group (—S—) for convenience's sake.

Table IV Solubility Parameter Differences of Polymer and Solvent

| Polymer | Solvent | Δ_{total}^a |
|---------|---------|--------------------|
| BD | NMP | 3.04 ^b |
| BD | DMSO | 5.34 |
| BO | NMP | 2.68 |
| BO | DMSO | 5.37 |

^a $\Delta_{total} = [(\delta_{dp} - \delta_{ds})^2 + (\delta_{pp} - \delta_{ps})^2 + (\delta_{hp} - \delta_{hs})^2]^{1/2}$, the latter subscript in each square term; p = polymer; s = solvent.

^b Solubility parameters were calculated using Hoy's method (see Ref. 33) and for good solubility Δ_{total} must be smaller than 5.

and E_{hi} factors, even though the safest way for the evaluation of total solubility parameter (δ) is to take average values calculated from Hoftyzer and Van Krevelen's method and Hoy's method.

According to Hildebrand, as a prerequisite for the solubility of a polymer in a solvent, the solubility parameter difference, $(\delta_p - \delta_s)^2$, must be as small as possible.²² Particularly, mutual solubility of polymer and solvent is more important than that the state of polymer and solvent are $\delta_p = \delta_s$ and only occurs if the degree of hydrogen bonding is about equal. Therefore, more contributing factors, in the case of BTDA-based polyimide/NMP or DMSO, might be the complexation capability between PIs and solvents.

Frayner³⁴ reported on the very large energetic interaction behaviors between different PIs and solvents due to hydrogen bonding. Bower and Frost³⁵ and Brekner and Feger³⁶ investigated the formation of the 4/1 complex of DMAC/PAA and NMP/PAA, respectively. Brekner and Feger also reported that the decomplexation energy was about 55 kJ/mol during cycloimidization.³⁶ The chemical interaction of PAA/solvents has been revealed by Hodgkin³⁷ and Brekner and Feger.^{38,39} Painter et al.⁴⁰ kinetically proved that the hydrogen-bonding interaction in polyamic acid could be strongly affected by the thermal curing steps using association models of acid/acid, amide/amide, and acid/amide and FTIR measurement.⁴¹

On these bases, the calculation of interaction parameters of PAAs and solvents were carried out to interpret the swelling systems of PIs and solvents. Hoy noticed that Δ_{total} should be less than 5 to obtain a good solubility.³³ Our results and analysis on our polymers and solvents coincide well with his criteria (see Table IV). Furthermore, when the swelling of BD-70 was compared with BD-100 at 80°C [see Fig. 2(a) and (b)], the former had more complexation sites resulting from the hydrogen bonding of the re-

maining amic acids than the latter possessed, leading to the larger solvent uptake of the former. Since the interaction of PAA/NMP was stronger than that of PAA/DMSO at 80°C, in both PAAs, the PAA/NMP system could form a stable complex combination.¹⁹⁻²² Swelling of BD-70 with NMP or DMSO are believed to start at the segments of uncured amic acid in backbones followed by the dissolution of swollen film.

The amide bond in NMP is known to form a miscible complex with amide and free acid bonds in PAA segments due to the strong hydrogen bonding.^{35,36} The carbonyl group in BTDA might be weak complex sites such that the carbonyl group could interact with the electron unpaired nitrogen in the amide bond of NMP and the same amide group could act as an electron-donating group.⁴² However, the sulfoxide group in DMSO is a somewhat electron-withdrawing group. Therefore, BTDA-based PAA had a complementary relationship with NMP in that the electron acceptor-donor system was well combined. But there has been no publication about clear kinetic studies of complexation of PAA/DMSO even though the sulfoxide group in DMSO might form hydrogen bonding with PAA.

Figure 3(b) and (c) exhibits profiles of the weight gain measured as a function of time and square root of time for BO-96 PI film in NMP at 117°C. The amount of weight uptake was linear with time initially and equilibrated after 420 min. From the sigmoidal curve of square root of time vs. weight gain, the swelling behaviors are thought to be Case II diffusion, i.e., non-Fickian behaviors.^{12,32,43-45}

Figure 4 displays the weight uptake of BO-96 in

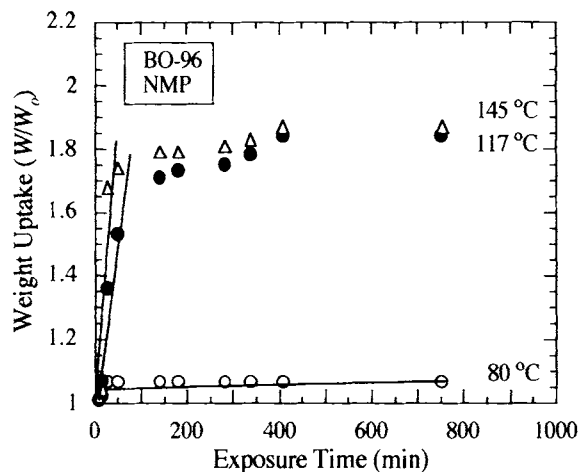


Figure 4 Dependence of swelling temperature on uptake of NMP in BO-96 PI measured at (○) 80°C, (●) 117°C, and (△) 145°C.

NMP as a function of time measured at three different swelling temperatures: 80, 117 and 145°C. At 80°C, the swelling behaviors of the BO-96 film showed very low weight gain of about 1.08. The same film considerably took NMP at over 117°C and then converged into approximately 1.8 ± 0.2 . Linear diffusion behaviors as a function of the swelling temperature was observed until about 200 min in exposure time. It should be noted that the swelling of liquid penetrants generally increases with temperature due to the solvent action as discussed by Hopfenberg and Frisch.⁴⁶

All the polymers in the solid state often exhibited a so-called secondary relaxation transition besides the main chains, namely, the softening glass transition temperature.⁴⁷⁻⁴⁹ In the case of BTDA/ODA PI having two flexible spacers, i.e., the carbonyl group in BTDA and the ether group in ODA, two relaxation behaviors over room temperature can be detected using a dynamic mechanical analyzer.⁵⁰ They are similar to the molecular motions of PMDA/ODA PI,⁴⁷ i.e., α (417°C),^{47,51} β (77–127°C),^{47,51,52} and γ (–73–0°C)^{51,52} peaks caused by relaxations of main chains, interplane slippage between aromatic and imide rings, and water absorbed, respectively. Among the relaxations of cured BTDA/ODA PI (BO-96), α and β dispersions were detected at about 290 and 120°C, respectively, measured by a DMTA (dynamic mechanical thermal analyzer, DuPont Model 983, 1 Hz, 5°C/min, N₂ gas flow = 200 cc/min).⁵⁰

Molecular chains of amic acids of BO-96 PI film form a weak complex between PAA and NMP or DMSO due to high content of imide rings detected by the FTIR measurement. From the DMTA result and our experimental data of diffusion on PI and the solvent system, the large amount of solvent uptake of BO-96 film at 115 and 145°C could be caused by the β relaxation of the oriented imide chain because the temperature of β relaxation (ca. 120°C) was similar to the swelling temperatures (115 and 145°C) and, thus, this molecular motion combined with the β relaxation can affect the swelling amount of solvent of BO-96 PI film. Therefore, the solvent uptake sharply increased because of the solvent-induced and thermally stimulated molecular surroundings caused by rapid solvent induction into the film and chemical complexation in the smaller region of amic acid.

Dimensional changes of swollen anisotropic PI film was caused mainly by the thickness increase as a normal direction to substrate rather than changes in lateral dimension of PMDA/ODA film.¹² We re-examined the dimensional variation in weight up-

take, thickness, and lateral increase of BO-96 PI film at 80°C, as shown in Figure 5. The increase of weight uptake is caused mainly by the thickness increase perpendicular to the substrate surface or axes of orientated macromolecules.^{12,32}

Figure 6 compares the effect of imide content of PI on the linear kinetics. We can see that the higher the imide content the lower the amount of sorption uptake. This phenomenon can easily be inferred from the fact that the complex site diminished with the increase of the formation of imide rings.

Figure 7 shows the swelling behaviors as a function of the thickness of BTDA/ODA films. Particularly, thin film less than 20 μm in thickness gained solvent rapidly. The thinner the PI film, the shorter the introduction time of solvents into the film and, thus, the equilibration region can be promptly formed because of the advancing sharp front meeting each other within a shorter time (in this case, about 200 min).

Isotropic BTDA/ODA PI film prepared (80°C, 1 h; then stripped off; cured continuously at 200°C for 1 h and at 300°C for 1 h; thickness = 35 μm) under a free-standing state (no substrate) was not swollen after long exposure time even if the amic acids existed, whereas anisotropic BTDA/ODA film swollen in NMP after 2500 min had a coarse and rubbery surface caused by plasticizing effects of the large amount of induced solvents (see Fig. 8). Thickening of the plasticization could lessen the densified, vitrified, and formed ordered phases of BO-96 PI film.³⁹ But the isotropic film maintained a glassy state similar to the initial surface state and no change of weight uptake could be found. There-

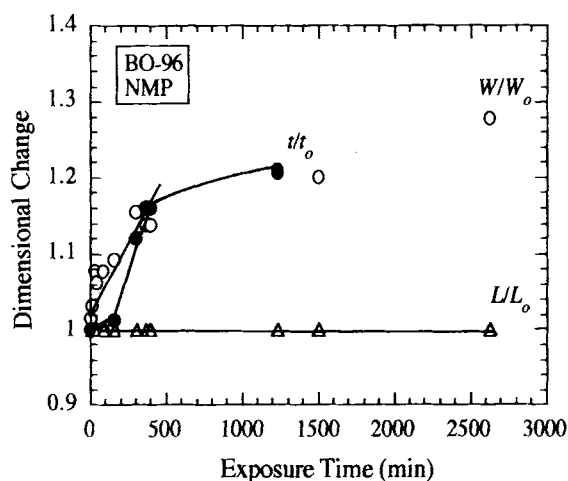


Figure 5 Dimensional changes [(○) weight uptake: W/W_0 ; (●) thickness increase: t/t_0 ; (△) lateral change: L/L_0] of BO-96 film after swelling in NMP for 2600 min.

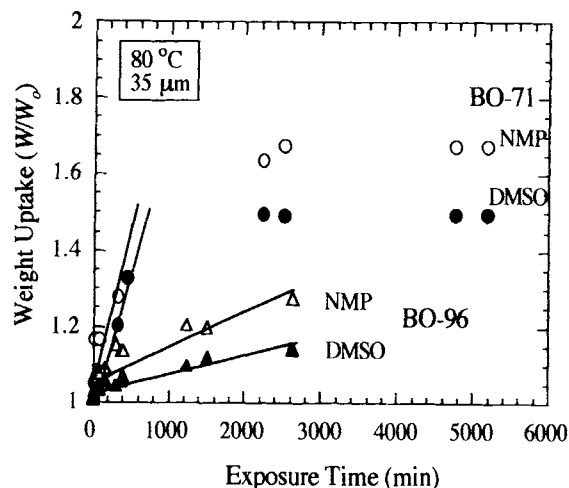


Figure 6 Effect of imide content and solvents on the swelling behaviors of BO-71 in (○) NMP and (●) DMSO and (△) BO-96 film in NMP and (▲) DMSO measured at 80°C.

fore, we could assure that the two solvents did not permeate into isotropic films and that the removal of the PAA prior to imidization followed by the thermal process at the no-substrate state had no room for preferential orientation or ordering.^{10,12,32,39}

BTDA/ODA PI molecules can be oriented from the interface of the glass plate or silicon wafer substrate. Particularly, the dense layer of in-plane orientation in an asymmetric structure may vary by the thermal treatment condition for cycloimidization, i.e., one-step heating up or stepwise heating up to a desired high temperature. We are underway in investigating effects of the degree of orientation in

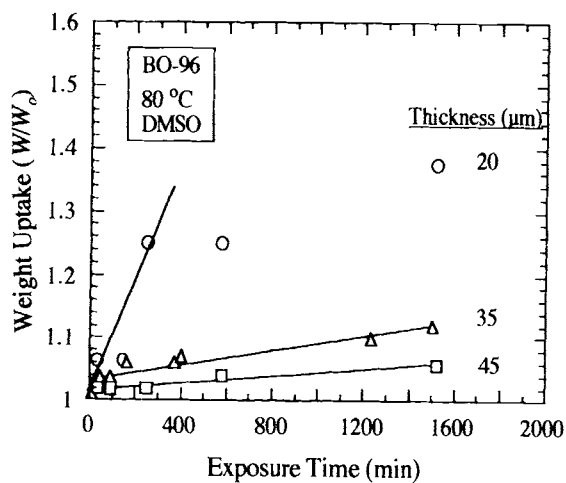


Figure 7 Effect of thickness on the uptake of DMSO in BO-96 PI film; thickness = (○) 20, (△) 35, and (□) 45 μm in DMSO.

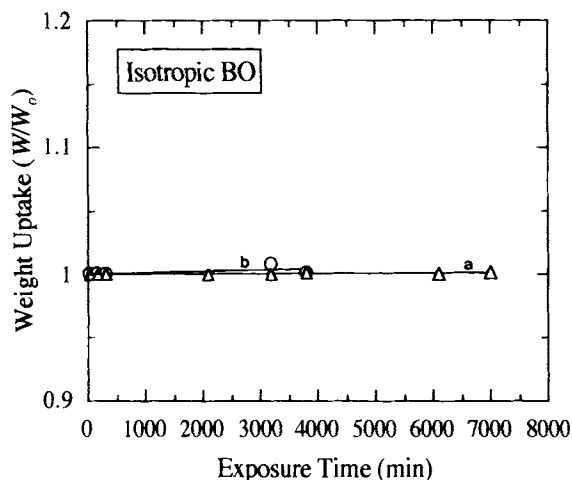


Figure 8 Swelling behaviors of isotropic BTDA/ODA PI films in (a) DMSO and (b) NMP.

the asymmetric structure using mechanical properties since the different imidization processes will produce the variance in stiffness and elasticity of in-plane oriented PI molecules. Isotropic and anisotropic PI films are also expected to have different molecular motion caused by a difference of the degree of orientation and molecular aggregation.^{30,31,39,52} Further studies will be continuously carried out using a dynamic mechanical analyzer to investigate the segmental molecular motion of PI molecules and examine the effect of local motion and relaxation of a rigid backbone on diffusion kinetics, particularly dependent on the thermal curing history for cycloimidization. The physicochemical diffusion properties caused by the difference of degree of orientation, internal stress, and annealing effects will also be reported soon.

CONCLUSION

The diffusion behaviors of BTDA/DDS and BTDA/ODA PI films showed a linear relationship with time and the Case II mechanism. PI films of the BTDA system had an affinity to NMP rather than to DMSO. The solubility parameter difference between BTDA-based PIs and NMP is less than 5, which explains the good solubility in NMP rather than in DMSO. Since the interaction of PAA/NMP is stronger than that of PAA/DMSO at 80°C, the PAA/NMP system could form a stable complex combination. The swelling of PI with solvents is believed to start at the segments of uncured amic acid in the backbones, followed by the dissolution of swollen film. As imide contents of PI increase, the

solubility diminishes due to the decreased complexation sites upon the formation of imide rings. The solvent uptake of the anisotropic film resulted mainly from the thickness increase normal to a substrate. The weight gain of the BTDA/ODA PI film increased with swelling temperature but decreased with film thickness and imide content via the Case II swelling mechanism. Isotropic films prepared by the no-substrate state were not diffused regardless of penetrants because of maintaining the glassy state. From these phenomenological results, thermodynamic aspects of front velocity, induction time, and internal stress combined with molecular motion and relaxation behaviors of anisotropic and isotropic films should be further considered to compare behaviors of segmental motion with diffusion kinetics of stiff PI molecules.

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