

Water Diffusion Studies in Polyimide Thin Films

JONGCHUL SEO, HAKSOO HAN

Department of Chemical Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-Gu, Seoul 120-749, South Korea

Received 29 August 2000; accepted 21 December 2000

ABSTRACT: The water diffusion behaviors and activation energies of PDA- and ODA-based polyimide thin films were quite dependent on both the chemical structure and the morphological structure in the films. The water diffusion coefficients of polyimide thin films increased with increasing temperature. The activation energies varied in the range of 5.81 to 9.27 kcal/mol and were relatively higher for the PDA-based polyimide thin films than for the corresponding ODA-based polyimide thin films. For the PDA- and ODA-based polyimide films, the differences in the morphological structures and the chemical affinity to water molecules might be reflected directly on the water diffusion behaviors. The PDA-based polyimide films exhibited a relatively more ordered morphological structure (high crystallinity and good in-plane orientation) than that of the corresponding ODA-based polyimide thin films, which may serve as impenetrable obstacles for the water diffusion in the out-of-plane direction. Consequently, it may lead to a relatively slower water diffusion and high activation energy in the PDA-based polyimide thin films. Additionally, the PDA-based polyimide films with relatively lower chemical affinity showed relatively low diffusion coefficients and high activation energies. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 731–737, 2001

Key words: diffusion coefficient; activation energy; polyimide films

INTRODUCTION

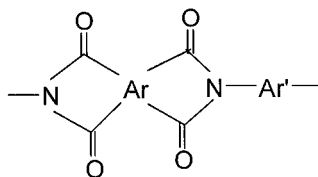
High-temperature aromatic polyimides are important materials for the electronic industry because of their high thermal stability, excellent mechanical toughness, and relatively high dielectric strength.^{1–4} However, the ease with which water diffuses through these materials is a recurrent issue of concern.^{5–8} In electronic devices this leads to reliability problems, such as displacement, package crack, delamination, loss of adhesion, potential corrosion, and mechanical failures in thin films. Consequently, studies focusing on

the water diffusion and state in polyimide films have been reported in the literature.^{8–11} Many studies have been concerned with the influence of backbone chemistry on the water diffusion; however, the water diffusion in polyimide films is strongly dependent on the morphological structures in films, which are remarkably sensitive to polymer chain rigidity and chemical backbone structure. The physical properties of a polyimide, particularly degree of crystallinity, chain orientation, and packing order, are primarily dependent on the polymer chain rigidity. The degree of order in polymer molecules can generally be described as semicrystalline or amorphous.^{12–14} The properties of these two classes of polymers with respect to the water diffusion can be expected to be significantly different.

In this study, we have chosen six different polyimides prepared from two diamines and three

Correspondence to: H. Han (E-mail: hshan@yonsei.ac.kr)
Contract grant sponsor: Korea Science and Engineering Foundation.

Journal of Applied Polymer Science, Vol. 82, 731–737 (2001)
© 2001 John Wiley & Sons, Inc.



	PMDA-PDA	PMDA-ODA	BPDA-PDA	BPDA-ODA	BTDA-PDA	BTDA-ODA
Ar						
Ar'						

Figure 1 Chemical structures of polyimides.

dianhydrides (see Fig. 1). Water diffusion behaviors and activation energies for polyimide thin films were gravimetrically investigated^{15–20} and interpreted in terms of the chemical structure and the morphological structures in films. The morphological structures in films were investigated by wide-angle X-ray diffraction and prism-coupling analyses.

EXPERIMENTAL

Materials and Film Preparation

Poly(1,4-phenylene pyromellitic acid) (PMDA–PDA PAA) solution was prepared under nitrogen atmosphere by slowly adding PMDA to PDA in anhydrous NMP, as described elsewhere.^{1–3,16,18} The resulting solution had a solid content of 15 wt %. Other poly(amic acid)s were prepared in the same manner as the PMDA–PDA precursor solution was synthesized: PMDA–ODA PAA, BPDA–PDA PAA, BPDA–ODA PAA, BTDA–PDA PAA, and BTDA–ODA PAA (see Fig. 1). Diamine and dianhydride monomers were purchased as commercial products [Aldrich Chemicals (Milwaukee, WI) and Chriskev Co.] and purified by sublimation under reduced pressure before use.

All of the polyimide precursors were spin-coated on silicon (100) substrates. Coated wafers were prebaked at 80°C for 30 min on a hot plate. The prebaked samples were then placed in a curing oven and cured by the following cure schedule: 150°C/30 min, 230°C/30 min, 300°C/30 min, and 400°C/60 min. The ramping rate was 2.5°C/min and the cooling rate was 2.0°C/min for the curing

process. Film thickness was measured by using a surface profiler (Model P-10; Tencor Instruments Co.). Then, the cured films were taken off from the substrates with the aid of deionized water and washed with distilled water several times. The fully cured films were cut into rectangular pieces approximately 10 × 15 mm and fully dried in a vacuum to use for the water diffusion measurements.

Measurements

For polyimide thin films, the water diffusion isotherms were gravimetrically measured at various temperatures of 5–60°C, using a Thin Film Diffusion Analyzer (Model D-200; Cahn Instruments), as described in previous studies.^{15–20} All the isotherms for the water diffusion were analyzed with a Fickian diffusion model^{21,22} as follows:

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

where $M(t)$ is the water sorption at time t , $M(\infty)$ is the water sorption at $t = \infty$, D (cm²/s) is the diffusion coefficient, and L is the film thickness, respectively. The diffusion coefficient D was estimated by best-fitting the measured water sorption isotherms with eq. (1).

Wide-angle X-ray diffraction (WAXD) patterns (transmission and reflection modes)^{23,24} were ob-

tained by using a wide-angle goniometer (Model RINT 2000; Rigaku Co., Japan) with monochromator (flat crystal type). The CuK_α radiation source ($\lambda = 1.54\text{\AA}$) was operated at 40 kV and 40 mA and all the measurements were carried out in the $\theta/2\theta$ mode with the diffraction vector both normal to and in the plane of the films. The 2θ scan data were collected in the range of $5\text{--}60^\circ$ at 0.02° intervals with a scan speed of $0.3\text{--}0.5^\circ \text{min}^{-1}$. In addition, the refractive indices were measured using a prism coupler (Model 2010; Metricon Inc.) with a He-Ne laser light. All the measurements were performed using a cubic zirconia prism of $n_{\text{TE}} = n_{\text{TM}} = 2.1677$ at $\lambda = 632.8 \text{ nm}$ wavelength. Here, the laser light is polarized into the direction either parallel to the film plane (TE mode) or perpendicular to the film plane (TM mode). Here, the resolution of refractive index was ± 0.0005 .

RESULTS AND DISCUSSION

The water diffusion isotherms for polyimide thin films were gravimetrically investigated over the temperature ranges of $5\text{--}60^\circ\text{C}$ and are depicted in Figure 2. All the diffusion isotherms were reasonably well fitted to a Fickian diffusion model, regardless of temperature and morphological heterogeneities attributed to the ordered and disordered phases in films.^{12–14} It shows that the diffusion behavior of small molecules in polymers should be patterned after a Fickian diffusion model, below the glass-transition temperature of the host. Thus, the diffusion coefficient was simulated with eq. (1) and is depicted in Figure 3(a) as a function of temperature.

The diffusion coefficient changed from 0.5 to $6.9 \times 10^{-10} \text{ cm}^2/\text{s}$ for the PMDA-PDA film and from 4.7 to $27.5 \times 10^{-10} \text{ cm}^2/\text{s}$ for the PMDA-ODA film, apparently increased with increasing temperature. The other polyimide films, BPDA-PDA, BPDA-ODA, BTDA-PDA, and BTDA-ODA, showed the same trends in the diffusion coefficients as those of PMDA-PDA and PMDA-ODA films, which may indicate that the polymer chains at higher temperatures can be more mobile or flexible and then make water molecules more penetrable, resulting in the increase of diffusion coefficient.^{25,26} However, the effect of temperature on the diffusion coefficient was more significant for the ODA-based polyimide films than for the corresponding PDA-based polyimide films, which may be caused by more enhanced

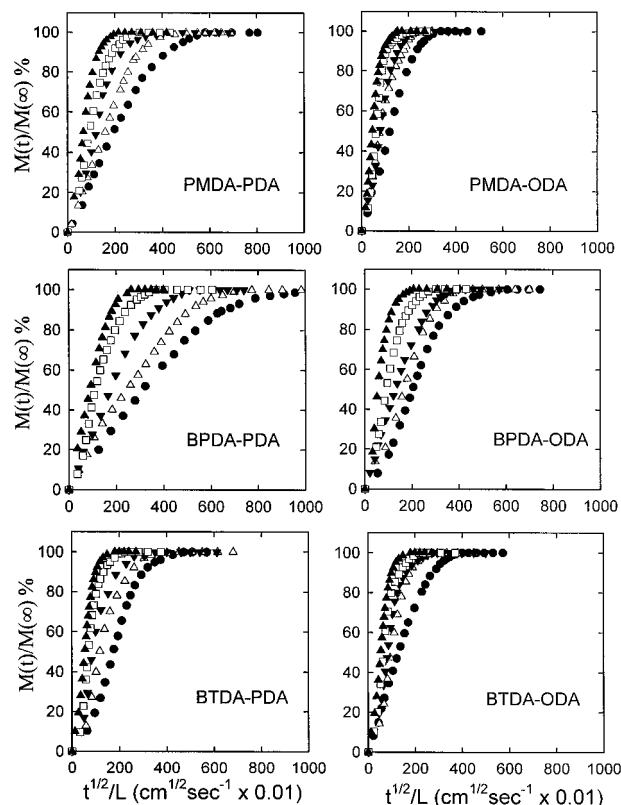


Figure 2 Water diffusion isotherms for polyimide thin films at various temperatures: (●) 5°C , (Δ) 15°C , (∇) 25°C , (\square) 40°C , and (\blacktriangle) 60°C .

mobility of polymer chains in the ODA-based polyimide films with increasing temperature.¹⁹ In addition, the diffusion coefficients over the temperature range of $5\text{--}60^\circ\text{C}$ were relatively higher in the ODA-based polyimide films, which indicates that it is more difficult for water molecules to diffuse through the PDA-based polyimide chains, thus requiring more energy (i.e., higher activation energy) for the water diffusion.

The activation energy for water diffusion is needed to enable water molecules to diffuse through polymer chains.^{21,27} The activation energy was calculated from the diffusion coefficients on the basis of the Arrhenius form by fitting the dependence of the logarithm of the diffusion coefficient on reciprocal temperature. As shown in Figure 3(b), the plots of $\ln D$ versus $1/T$ exhibited a fairly linear relationship, which implies two things: (1) the diffusion kinetics of water molecules does not change with varying temperatures²⁷ and (2) polyimide films may not undergo a change in the morphology or a shift of glass transition by the plasticization action of the diffused water molecules.²⁸

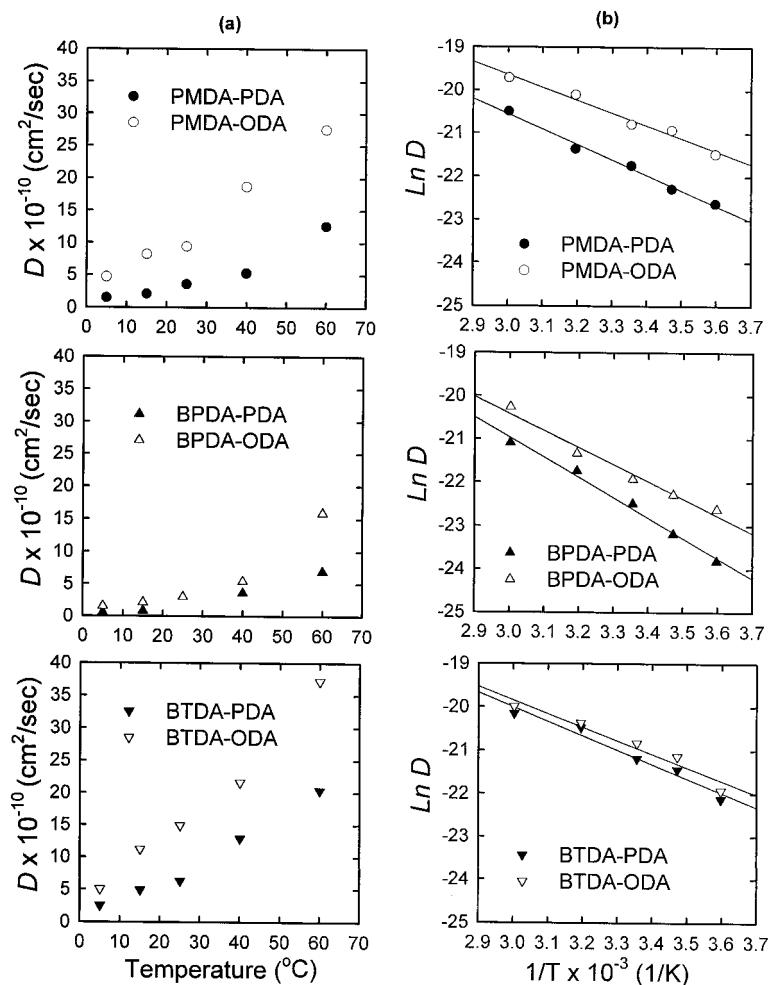


Figure 3 (a) Diffusion coefficients as a function of temperature and (b) Arrhenius plots of the diffusion coefficient in polyimide thin films.

The activation energies of polyimide thin films are summarized in Table I. These results are within the spectrum of those previously reported.^{2,25} The activation energies were strongly dependent on the chemical structure of

Table I Activation Energies of Polyimide Thin Films

Polyimide Structure	Film Thickness (μm)	Activation Energy (kcal/mol)
PMDA-PDA	12.20	7.63
PMDA-ODA	11.02	5.81
BPDA-PDA	15.23	9.27
BPDA-ODA	12.80	7.90
BTDA-PDA	11.02	6.70
BTDA-ODA	13.02	6.14

the polyimide and increased in the order PMDA-ODA \sim BTDA-ODA $<$ BTDA-PDA $<$ PMDA-PDA \sim BPDA-ODA $<$ BPDA-PDA. These results are in good agreement with those of the diffusion coefficients. Regardless of dianhydride structure, PDA-based polyimide films showed relatively higher activation energy than that of the corresponding ODA-based polyimide films, which indicates the difficulty for water molecules to diffuse through the PDA-based polyimide chains. In the present study, all of the polyimide thin films were so thin that the water diffusion occurred preferentially in the out-of-plane direction (perpendicular to the film surface), with a negligible amount through the edges. Thus, it is speculated that the water diffusion may be considerably dependent on the in-plane morphological structure in the polyim-

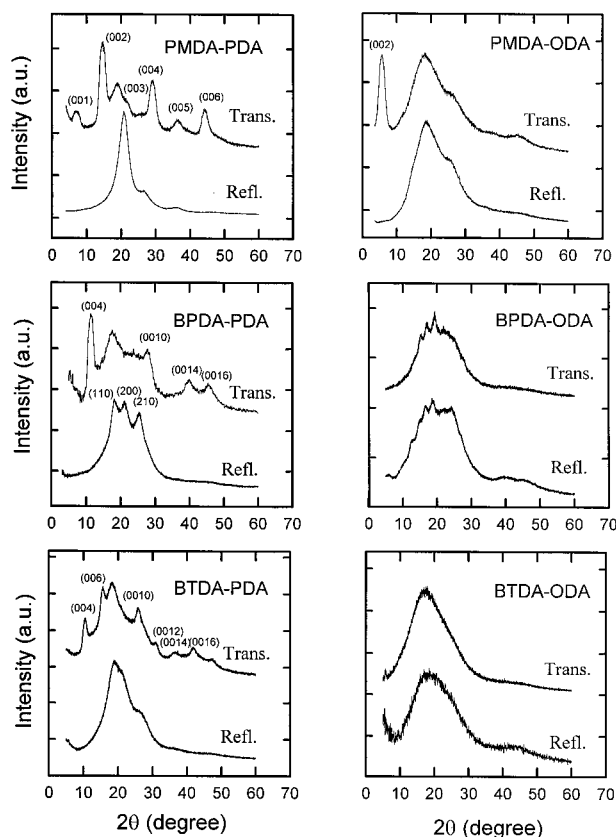


Figure 4 WAXD patterns of polyimide thin films.

ide films, which are closely related to the chemical structure of a polymer.^{16–20,23,24}

Depending on the chemical structure, the difference in the water diffusion behaviors and activation energies might result from some variations in the morphological structures in films. Generally, the degree of ordering and crystallinity in polyimide films depend on the kinked group and the way samples are prepared.^{1,2} Compared with the structure of the PDA diamine, that of the ODA diamine in the polyimide has a kinked ether linkage unit per repeating chain unit (see Fig. 1), leading to relatively amorphous and less-ordered structure in the ODA-based polyimide thin films. In this study, all samples were prepared from the same sample preparation method. Thus, the morphological structure in polyimide films may be solely dependent on the chemical structure. Some information about the morphological structures can be obtained from WAXD patterns of the polyimide films, as shown in Figure 4. Here, the transmission pattern gives structural information for the film plane, whereas the reflection pattern presents structural information for the out-of-film plane.^{15–20,29}

All of the PDA-based polyimide thin films, PMDA-PDA, BPDA-PDA, and BTDA-PDA showed (00 l) diffraction peaks in the transmission pattern, corresponding to the molecular order along the chain axis. In contrast, (00 l) diffraction peaks in the transmission pattern were not apparent for the ODA-based polyimide thin films. PMDA-ODA film showed only one sharp (002) diffraction peak at a low angle of $2\theta = 5.74^\circ$ and BPDA-ODA film showed multiple diffraction peaks on the big amorphous halo peak in the diffraction patterns over the angle range of 10 to 30° . This indicates that the PDA-based polyimide film has higher crystallinity and better in-plane orientation than that of the corresponding ODA-based polyimide films. Except BPDA-PDA and BPDA-ODA films, the reflection patterns of polyimide films exhibited only one amorphous halo peak. This may indicate that polyimide films, except BPDA-PDA and BPDA-ODA films, have poor packing order. BPDA-PDA film showed three (hkl) peaks in the reflection pattern, such as (110), (200), and (210), and BPDA-ODA film showed multiple diffraction peaks on the big amorphous halo peak in diffraction patterns over the angle range of 10 to 30° (2θ), indicating good packing order in films.

In addition to the characteristic X-ray diffraction patterns in polyimide films, the mean intermolecular distance, which may be a critical factor for water diffusion,^{16–19} was calculated from the characteristic transmission and reflection peaks, as shown in Table II. The ODA-based polyimide thin films showed relatively higher mean intermolecular distance than that of the corresponding PDA-based polyimide thin films, indicating that polymer chains of the PDA-based polyimide thin films are more or less well oriented and ordered in the film plane.

These WAXD patterns indicate that the PDA-based polyimide thin films had relatively higher crystallinity structure and good in-plane orientation than that of the corresponding ODA-based polyimide thin films.

The molecular in-plane orientation of polymer chains was further studied by using the prism coupler, as shown in Table II. All of the polyimide thin films showed larger in-plane refractive index (n_{xy}) than out-of-plane refractive index (n_z), regardless of their chemical structures. This indicates that all of the polyimide thin films in this study have positive birefringence and polymer chains are preferentially aligned in the film plane.^{15,16,19} In comparison, n_{xy} and the average refractive index (n_{av}), indicating the in-plane ori-

Table II Mean Intermolecular Distances and Refractive Indices of Polyimide Thin Films

Polyimide Structure	Film Thickness (μm)	Mean Intermolecular Distance ^a		Refractive Indices at 632.8 nm			
		In-Plane (\AA)	Out-of-Plane (\AA)	In-Plane Refractive Index (n_{xy})	Out-of-Plane Refractive Index (n_z)	Average Refractive Index ^b (n_{av})	Birefringence ^c (Δ)
BPDA-ODA	12.20	4.78	4.26	1.8224	1.5827	1.7438	0.2397
BPDA-ODA	11.02	4.94	4.81	1.7219	1.6390	1.6934	0.0829
PMDA-ODA	15.23	4.81	4.79	1.8507	1.6147	1.7720	0.2360
PMDA-ODA	12.20	4.90	4.90	1.7474	1.6807	1.7252	0.0667
BTDA-ODA	11.02	4.90	4.80	1.7730	1.6349	1.7270	0.1381
BTDA-ODA	13.02	5.23	4.88	1.6922	1.6763	1.6869	0.0053

^a Calculated from the peak maximum of amorphous halos in WAXD patterns.

^b $n_{av} = (2n_{xy} + n_z)/3$.

^c $\Delta = n_{xy} - n_z$.

entation of polymer films, increase in the order BPDA > PMDA > BTDA for the PDA- and ODA-based polyimide thin films. In addition, the PDA-based polyimide films showed relatively higher n_{xy} and n_{av} than that of the corresponding ODA-based polyimide films, which indicates that the PDA-based polyimide films are preferentially aligned in the film plane. Specifically, the relatively low average refractive indices in BTDA-ODA films may be ascribed to the additional polarizations contributed by the ether and carbonyl linkages on the backbones. These refractive index results indicate that the molecular in-plane orientation increased in the order BTDA-based polyimides < PMDA-based polyimides < BPDA-based polyimides. Moreover, the PDA-based polyimide films have better in-plane orientation than that of the corresponding the ODA-based polyimide films. The results observed in the refractive indices of polyimide thin films are fully consistent with those in the WAXD patterns.

It is well known that highly packed and crystalline phases serve as impenetrable obstacles that diminish the volume available for water diffusion^{26,27} because distances between polymer chains are too small to allow water molecules to pass through them. It means that the high degree of in-plane orientation, high crystallinity, and small mean intermolecular distance will make it more difficult for water molecules to diffuse in the out-of-plane direction, resulting in low diffusion coefficients and high activation energies in the well-ordered structure polymers. The above-mentioned morphological differences in the PDA- and

ODA-based polyimide films might be reflected directly on the water diffusion behaviors. The PDA-based polyimides exhibited a relatively more ordered morphological structure (i.e., higher in-plane orientation and higher degree of crystalline structure) than that of the corresponding ODA-based polyimides, consequently leading to a relatively more rapid water diffusion and low activation energy in the ODA-based polyimide thin films.

In addition to the morphological structures of polyimide thin films, the water diffusion behaviors could be interpreted by the chemical structure.^{15,20,28} Compared with the chemical structure of PDA diamine, ODA diamine has an ether linkage (-O-) in the backbone, which can be treated as a relatively hydrophilic site for water molecules. Thus, the chemical affinity to water molecules increases in the order PDA < ODA. In view of chemical affinity, one may expect that the ODA-based polyimides show lower water diffusion than that of the corresponding PDA-based polyimide thin films. For the dianhydride structure, the chemical affinity to water increases in the order BPDA < PMDA < BTDA. This is in good agreement with the water diffusion behaviors of polyimide thin films. The PDA-based polyimide films with relatively lower chemical affinity showed relatively low diffusion coefficients and high activation energies. In the ODA-based polyimides, however, the activation energy for water diffusion showed some discrepancies, which may come from similar chemical and morphological structures in PMDA-ODA and BTDA-ODA.

CONCLUSIONS

The water diffusion behaviors and the activation energies were gravimetrically investigated for both PDA- and ODA-based polyimide thin films. The water diffusion coefficients of all of the polyimide thin films increased with increasing temperature. Activation energies varied in the range of 5.81 to 9.27 kcal/mol and were relatively higher for PDA-based polyimide thin films than for ODA-based polyimide thin films. For the PDA- and ODA-based polyimide films, the differences in the morphological structures in films and the chemical affinity to water molecules might be reflected directly on the water diffusion behaviors. The PDA-based polyimide films exhibited a relatively more ordered morphological structure (high crystallinity and better in-plane orientation) than that of the corresponding ODA-based polyimide thin films, consequently leading to relatively slower water diffusion and higher activation energy in the PDA-based polyimide thin films. Additionally, the PDA-based polyimide films with relatively lower chemical affinity showed relatively low diffusion coefficient and high activation energy.

This work was supported by the Center for Electronic Packaging Materials of Korea Science and Engineering Foundation.

REFERENCES

- Bessonov, M. I.; Zubkov, V. A. *Polyamic Acids and Polyimides: Synthesis, Transformations, and Structure*; CRC Press: Boca Raton, FL, 1993.
- Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
- Feger, C.; Khojasteh, M. M.; Htoo, M. S. *Advances in Polyimide Science and Technology*; Technomic: Lancaster, PA, 1993.
- Mittal, K. L. *Polyimides: Synthesis, Characterization, and Applications*; Plenum Press: New York, 1984.
- Thompson, L. F.; Willson, C. G.; Tagawa, S. *Polymers for Microelectronics: Resists and Dielectrics*; ACS Symposium Series 537; American Chemical Society: Washington, DC, 1994.
- Bellucci, F.; Khamis, I.; Senturia, S. D.; Latanision, R. M. *J Electrochem Soc* 1990, 137, 1778.
- Melcher, J.; Daben, Y.; Arlt, G. *IEEE Trans Electron Devices* 1989, 24, 31.
- Denton, D. D.; Day, D. R.; Priore, D. F.; Senturis, S. D. *J Electron Mater* 1985, 14, 119.
- Okamoto, K. I.; Tanihara, N.; Watanabe, H.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y.; Nakagawa, K. *J Polym Sci Part B Polym Phys* 1992, 30, 1223.
- Iler, L. R.; Laundon, C.; Koros, W. J. *J Appl Polym Sci* 1982, 27, 1163.
- Li, S. Z.; Chen, R. S.; Greenbaum, S. G. *J Polym Sci Part B Polym Phys* 1995, 33, 403.
- Isoda, I.; Shimada, H.; Kochi, M.; Kambe, H. *J Polym Sci Part B Polym Phys* 1981, 19, 1293.
- Russell, T. P. *Polym Eng Sci* 1984, 24, 345.
- Russell, T. P. *J Polym Sci Part B Polym Phys* 1984, 22, 1105.
- Han, H.; Seo, J.; Ree, M.; Pyo, S. M.; Gryte, C. C. *Polymer* 1998, 39, 2963.
- Seo, J.; Jeon, J.; Lee, C.; Park, S.; Han, H. *J Appl Polym Sci* to appear.
- Seo, J.; Han, H.; Lee, A.; Han, J. *Polym J* 1999, 31, 324.
- Seo, J.; Lee, A.; Lee, C.; Han, H. *J Appl Polym Sci* 2000, 76, 1315.
- Seo, J.; Jeon, J.; Shul, Y. G.; Han, H. *J Polym Sci Part B Polym Phys* 2000, 38, 2714.
- Seo, J.; Han, H. *Polymer* to appear.
- Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, 1976.
- Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic Press: London, 1968.
- Han, H.; Gryte, C. C.; Ree, M. *Polymer* 1995, 36, 1663.
- Ree, M.; Han, H.; Gryte, C. C. *J Polym Sci Part B Polym Phys* 1995, 33, 505.
- Van Alsten, J. G.; Coburn, J. C. *Macromolecules* 1994, 27, 3746.
- Papllham, W. P.; Brown, R. A.; Salin, I. M.; Seferis, J. C. *J Appl Polym Sci* 1995, 57, 133.
- Chang, Y. L.; Jou, J. H. *J Polym Sci Part B Polym Phys* 1994, 32, 2143.
- Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier Science: Amsterdam, 1990.
- Cullity, B. D. *Elements of X-ray Diffraction*, 2nd ed.; Addison-Wesley: London, 1977.