

Effects of Addition Orders on the Properties of Fluorine-Containing Copolyimides

LI REN,¹ FANSEN ZENG,¹ PING NING,¹ ZHIQUAN CHEN,¹ TZE-MAN KO²

¹ Institute of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China

² Department of Chemical and Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Received 28 April 1999; accepted 3 January 2000

ABSTRACT: A series of fluorine-containing copolyimides were synthesized by three different orders of addition of monomers. The fluorine-containing copolyimides were prepared by the reaction of 4,4'-diaminodiphenylmethane (DDM) with 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), and pyromellitic dianhydride (PMDA). The synthesis reactions of the copoly(amic acid)s (PA) were carried out by three different orders of addition of the monomers with different molar ratios of 6FDA to PMDA. The viscosity of the PA solution obtained by DDM-(6FDA+PMDA), that is, 6FDA and PMDA added simultaneously to DDM in *N*-methyl-2-pyrrolidinone (NMP), was higher than the other two addition orders (i.e., DDM-6FDA-PMDA and DDM-PMDA-6FDA). The viscosity decreased as the relative amount of 6FDA to PMDA increased. The copolyimides formed by different addition orders but the same 6FDA-to-PMDA molar ratios contained different properties, such as dielectric constant, moisture absorption, contact angle, and optical transparency. All of these copolyimides were insoluble in common organic solvents, such as NMP and tetrahydrofuran. Thermogravimetric analysis showed that the onset temperature of 8% weight loss decreased slightly as [6FDA] : [PMDA] increased. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3252–3258, 2000

Key words: fluorine-containing copolyimides; addition order; 4,4'-diaminodiphenylmethane (DDM); 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA); pyromellitic dianhydride (PMDA)

INTRODUCTION

Polyimides play an important role in modern, very large scale integrated circuit manufacturing and packaging. They possess a combination of properties, such as thermal stability, step coverage, processability, and resistivity, that are not available from other organic or inorganic materials.¹ Thus, polyimides are used increasingly by

the electronic industry as the interlayer dielectrics, passivation, and protective coatings in the integrated circuit fabrication. However, the commercially available polyimides have some disadvantages, such as low optical transparency, high dielectric constant, and high moisture absorption. Considerable attention has been devoted to the preparation of fluorine-containing polyimides because of their unique properties and high temperature performance. The incorporation of fluorine into the polyimide structures has been explored intensively in the past decade in order to fine-tune several properties for a particular interest.

Correspondence to: T.-M. Ko (chekotm@nus.edu.sg).

Journal of Applied Polymer Science, Vol. 77, 3252–3258 (2000)
© 2000 John Wiley & Sons, Inc.

Many new fluorine-containing monomers have been used to prepare new fluorinated polyimides.²⁻⁹ In addition, most work has concentrated on the incorporation of hexafluoroisopropylidene moieties (6F) into the polyimide structures, because significant property enhancements have been realized with the 6F functional groups, whereas other fluorinated monomers are not commercially available and are relatively difficult and expensive to synthesize. Fluorine incorporation has been found to generally lower the dielectric constant and moisture absorption so that desirable changes to optical properties and thermal stability are achieved in some cases. However, these new types of fluorinated polyimides generally have problems for interlayer insulation, such as poor solvent resistance and delamination between polyimide layers.

In order to remedy the disadvantages and to retain the advantages, copolymerization of polyimides was investigated. Several copolyimides were prepared by random, block, and alternating copolymerization techniques using either a diamine and two different dianhydrides or a dianhydride and two different diamines.¹⁰⁻²¹ However, most researchers only utilized a single order of addition of the monomers in the copolymerization reactions when they prepared for the different series of fluorine-containing copolyimides. According to Lee and coworkers,^{22,23} the microstructures of the reaction products could be very complicated because of the differences in reactivity between organic diamines and siloxane diamines and different reaction schemes used for the polycondensation reactions of these monomers. In copolymerization reactions, the orders of addition of the monomers are in fact very important. In this study, fluorinated copolyimides were synthesized with different additional orders and different relative amounts of 6FDA and PMDA. In addition, the properties of these copolyimides were investigated.

MATERIALS AND METHODS

Syntheses of Homopolyimides and Copolyimides

Figure 1 illustrates the chemical structures of the monomers that were used in the syntheses of the homopolyimides and copolyimides. Pyromellitic dianhydride (PMDA; 1,2,4,5-benzenetetracarboxylic anhydride) obtained from the Shanghai Chemical Reagents Purchasing Station was sub-

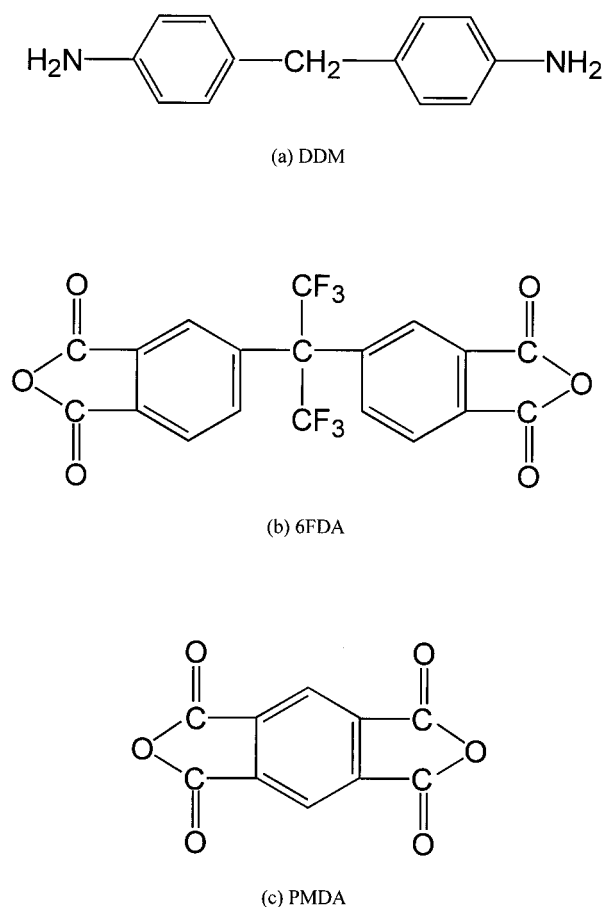


Figure 1 The chemical structures of (a) 4,4'-diaminodiphenylmethane (DDM), (b) 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), and (c) pyromellitic dianhydride (PMDA).

limed before use. 2,2'-Bis(3,4-dicarboxyphenyl) hexafluoropropane (6FDA) and 4,4'-diaminodiphenylmethane (DDM; 4,4'-methylenedianiline) obtained from the Aldrich Chemical Company (Milwaukee, WI) were used without further purification. *N*-methyl-2-pyrrolidinone (NMP) obtained from the BASF Company (Carrollton, TX) was also used without purification.

The poly(amic acids) (PA) were prepared in a three-necked flask with vigorous agitation by a magnetic stirring bar. For the homopolyimides, 0.0104 mol of the dianhydride (either PMDA or 6FDA) was added to 40 mL of NMP solution containing 0.0100 mol of DDM. For the copolyimides, three different addition orders were selected to form three different series of copolyimides:

1. DDM-6FDA-PMDA: A calculated amount of 6FDA was added to a solution of DDM in

NMP and was reacted for 1 h. Afterward, a calculated amount of PMDA was added.

2. DDM-(6FDA+PMDA): Calculated amounts of 6FDA and PMDA were added simultaneously to a solution of DDM in NMP.
3. DDM-PMDA-6FDA: A calculated amount of PMDA was added to a solution of DDM in NMP and was reacted for 1 h. Afterward, a calculated amount of 6FDA was added.

In the copolymerization reactions, the relative amounts of 6FDA and PMDA were not constant but the molar ratios of the total amounts of dianhydrides ($[PMDA] + [6FDA]$) to the diamine ($[DDM]$) were fixed at 1.04 : 1.00. The temperature was held at 30°C for 6 h in all cases. Thermal imidization was carried out by casting the PA solutions onto the glass plates and placing them in a vacuum oven. Then they were heated at 80°C for 3 h and sequentially heated at 100, 120, 150, and 200°C for 1 h in each heating step. Finally, the samples were cured at 300°C for 1 h in a convection oven under N_2 flow. The films synthesized were tough, transparent, and yellowish in appearance.

Measurements of Properties

Intrinsic viscosity measurement was performed to determine the relative molecular weights of PA in NMP solutions at a concentration of 0.5 g/dL. A Cannon-Ubbelohde viscometer was used at a bath temperature of 30°C. Fourier transform infrared (FTIR) spectra were collected with a Perkin-Elmer 1700 IR spectrometer (Norwalk, CT). Thermogravimetric diagrams were obtained with a thermogravimetric analyzer (Model 1090; DuPont, Wilmington, DE) at a heating rate of 10°C/min in N_2 . The dielectric constants of the polyimide films were obtained by measuring their capacitances with GenRad Precision RLC Digibridge Model 1689 (Concord, MA), equipped with 2.54-cm circular gold electrodes mounted in a brass dielectric cell at 25°C, 1 kHz, and 50% relative humidity.³

The optical transparency of the films was measured by Shanghai No. 3 Optical Instruments WGW Photoelectricity Diaphanometer with CIE Standard Illumination Source C. In the water absorption tests, the polyimide films were cut into 20 × 20-mm samples. The samples were dried at 105°C for 1 h and weighed. Afterward, they were kept in deionized distilled water at 25°C for 24 h and weighed again. Contact angle was measured using Xie-He CA-A contact angle instrument with

doubly deionized distilled water as the reference liquid. The solubility of polyimides was tested by immersing 2 wt % of the films in solvents and stored in small capped glass vials for 1 day.

RESULTS AND DISCUSSION

The viscosity of the PA solutions is affected by the purity of the monomers and solvents, temperature, and moisture content. Bower and Frost²⁴ found that the order of addition of the monomers was an important factor for the extent of polymerization. Addition of a diamine to a PMDA solution produced a lower molecular weight PA solution than when it was prepared in the reverse order of addition. However, Volksen and Cotts²⁵ stated that monomer concentration and addition sequence had no effect on the molecular weight of the PA solutions when they were prepared from highly purified PMDA and 4,4'-oxydianiline in freshly distilled NMP with the exclusion of atmospheric moisture.¹⁶ Lee et al.^{22,23} concluded that the microstructures of the resulting products were different when different orders of addition were used for the polycondensation reactions of DDM with 6FDA and PMDA, because of the structural differences of 6FDA and PMDA. In copolymerization, the order of addition of the monomers and comonomers is very important because there is a significant difference in the reactivity between 6FDA and PMDA. The number-averaged molecular weights of the copolymers and the extents of copolymerization reactions are mainly dependent on the molar ratios of diamines and dianhydrides existent at the instants of the copolycondensation reactions. Because the different orders of addition of the monomers give rise to different diamine-to-dianhydride molar ratios for the same reaction time, the extents of reactions as well as the molecular weights and microstructures of the copolyimides in the corresponding systems are thus different.

In this study, DDM was reacted with different quantities of dianhydrides (6FDA and/or PMDA) in the first hour. Consequently, the extents of polymerization and side reactions were different, and the molecular chains would have different binding patterns and terminal groups in each case. As a result, the different nature of the molecular chains formed in the first hour would lead eventually to differences in the overall extents of reactions and molecular weights.²⁶ As shown in Figure 2, the intrinsic viscosities of PA solutions

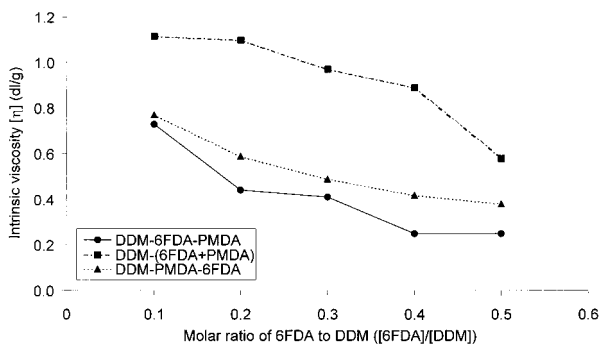


Figure 2 Effect of the molar ratio of 6FDA to DDM on the viscosity of the copoly(amic acid)s. Since $([6FDA] + [PMDA])/[DDM] = 1.04$ for all cases, the molar ratio of 6FDA to DDM was inversely proportional to the molar ratio of PMDA to DDM. Therefore, an increase of $[6FDA]/[DDM]$ equivalently represents an increase of $[6FDA]/[PMDA]$.

obtained by different addition orders were different. The intrinsic viscosities of the PA solutions of DDM-(6FDA+PMDA) were higher than those of the other two series of copolyimides. Because the molar ratios of diamines to dianhydrides in DDM-(6FDA+PMDA) were much closer to 1 : 1 than those of the other two series when the synthesis reactions began, the copolymerization in DDM-(6FDA+PMDA) could proceed to yield comparatively high-molecular-weight PA solutions, and the side reactions were relatively suppressed. Moreover, in all cases, the intrinsic viscosity decreased with the increase of the molar ratio of 6FDA to PMDA. The influences of 6FDA's molecular-chain structure on the copolymerization reactions as well as the molecular weights and viscosities of the resulting copolymers are still under investigation.

The PA was imidized via the conventional thermal route. A final curing temperature of 300°C was necessary for the removal of residual solvents and to ensure complete cyclization. Complete cyclodehydration by thermal imidization method was confirmed by the appearance of the characteristic imide-related IR absorption bands in 1770–1780 and 1710–1735 cm^{-1} as well as the disappearance of the amic acid band at 1535 cm^{-1} . FTIR also was used to characterize the structures of the copolyimides. In Figure 3, there is a new band centered at 1258 cm^{-1} that could be attributed to the $-\text{CF}_3$ moiety in the copolyimides. It is clear that 6FDA was incorporated into the polymers.

The thermal properties of homopolyimides and copolyimides were studied by thermogravimetric

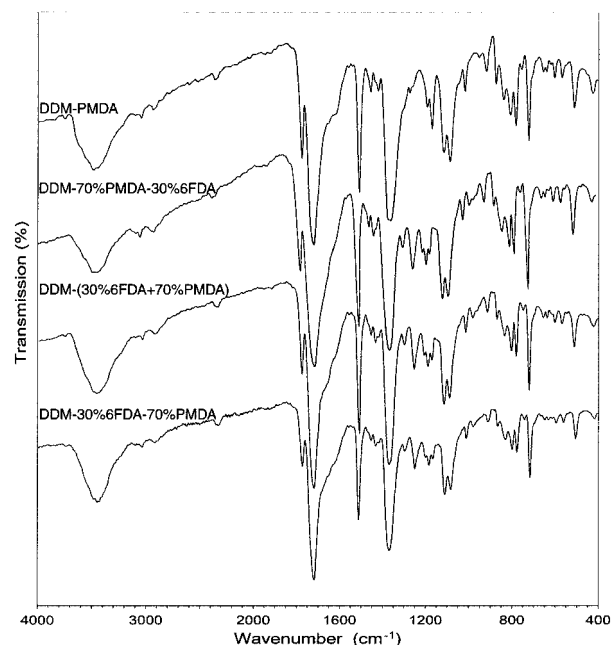


Figure 3 FTIR spectra of the DDM-PMDA homopolyimide and various fluorine-containing copolyimides.

analysis (TGA). In Figure 4, the initial weight losses from 25 to 130°C were due to solvent evaporation. The onset temperatures of 8% weight loss for DDM-PMDA, DDM-20%6FDA-80%PMDA, DDM-40%6FDA-60%PMDA, and DDM-6FDA were 564, 559, 549, and 542°C, respectively. Therefore, the DDM-PMDA homopolyimide film indicated higher thermal stability than all of the fluorine-containing homopolyimides and copolyimide films. In addition, the onset temperature of 8% weight loss decreased slightly as the molar ratio of 6FDA to PMDA increased.

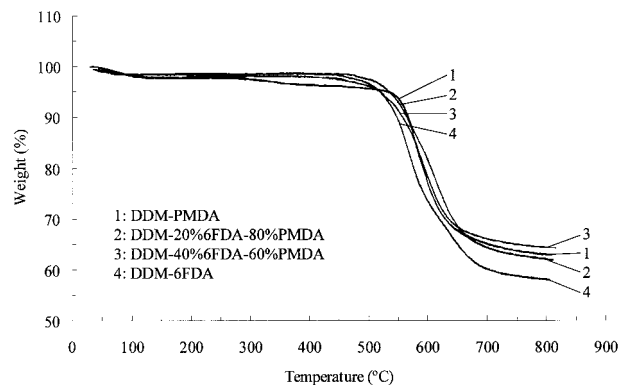


Figure 4 Thermogravimetric spectra for (a) DDM-PMDA, (b) DDM-20%6FDA-80%PMDA, (c) DDM-40%6FDA-60%PMDA, and (d) DDM-6FDA.

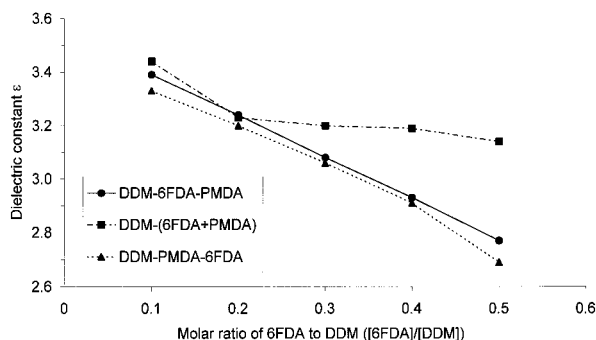


Figure 5 Effect of the molar ratio of 6FDA to DDM on the dielectric constant of the copolyimides. Since $([6\text{FDA}] + [\text{PMDA}])/[\text{DDM}] = 1.04$ for all cases, the molar ratio of 6FDA to DDM was inversely proportional to the molar ratio of PMDA to DDM. Therefore, an increase of $[6\text{FDA}]/[\text{DDM}]$ equivalently represents an increase of $[6\text{FDA}]/[\text{PMDA}]$.

The dielectric constant of the homopolyimide prepared from PMDA and DDM was found to be 3.83 and that of 6FDA and DDM was 2.68. Figure 5 shows the dielectric constants of the three series of copolyimides. The copolyimides of different addition orders gave rise to different dielectric constants, even though they were produced from the same molar ratios of 6FDA to PMDA. The dielectric constants of DDM-(6FDA+PMDA) copolyimides were the highest in the three different series of copolyimides. Because the dielectric constant is dependent on the polarizability of the medium, it is affected by the molecular weight, microstructure, and physical state of the material. In these experiments, the different addition orders would

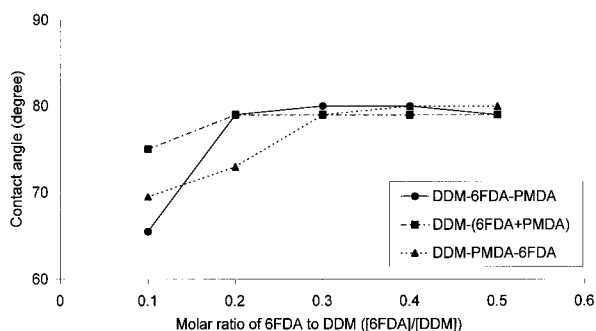


Figure 6 Effect of the molar ratio of 6FDA to DDM on the contact angle of the copolyimides. Since $([6\text{FDA}] + [\text{PMDA}])/[\text{DDM}] = 1.04$ for all cases, the molar ratio of 6FDA to DDM was inversely proportional to the molar ratio of PMDA to DDM. Therefore, an increase of $[6\text{FDA}]/[\text{DDM}]$ equivalently represents an increase of $[6\text{FDA}]/[\text{PMDA}]$.

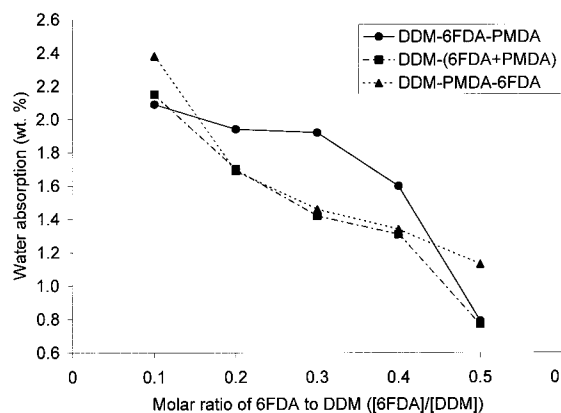


Figure 7 Effect of the molar ratio of 6FDA to DDM on the water absorption of the copolyimides. Since $([6\text{FDA}] + [\text{PMDA}])/[\text{DDM}] = 1.04$ for all cases, the molar ratio of 6FDA to DDM was inversely proportional to the molar ratio of PMDA to DDM. Therefore, an increase of $[6\text{FDA}]/[\text{DDM}]$ equivalently represents an increase of $[6\text{FDA}]/[\text{PMDA}]$.

produce copolyimides of very different microstructures and segmental sequences. In the DDM-(6FDA+PMDA) series of copolyimides, 6FDA and PMDA were well mixed before they were added simultaneously into the DDM solutions. As a result, 6FDA segments in DDM-(6FDA+PMDA) were much more randomly distributed in the copolyimide molecular chains than in DDM-6FDA-PMDA and DDM-PMDA-6FDA, because in the latter two systems DDM was reacted with either 6FDA or PMDA alone for an hour before the other component was added. Because of the different microstructures formed by the different addition orders, the copolyimides would have different dielectric constants even though they were produced from the same 6FDA-PMDA molar ratios. Furthermore, Figure 5 shows that the dielectric constants of all copolyimides decreased as $[6\text{FDA}]:[\text{PMDA}]$ increased. This confirmed that incorporation of fluorine-containing groups, such as $-\text{C}(\text{CF}_3)_2$ in polyimides would result in a decrease in the dielectric constant.

It is important for the electronics industry that the insulating polymers possess low water absorption rates and low moisture contents. The contact angle and moisture content of the DDM-PMDA homopolyimide were 52.5° and 3.33%, respectively. However, the contact angle and moisture content of DDM-6FDA homopolyimide were 80° and 0.72%, respectively. As shown in Figure 6, the DDM-(6FDA+PMDA) copolyimide films, in which the 6FDA segments were much more ran-

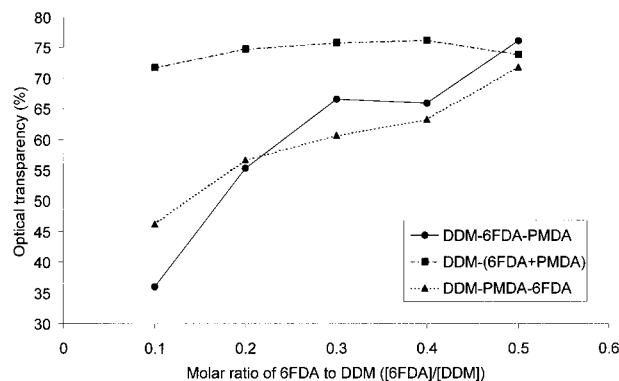


Figure 8 Effect of the molar ratio of 6FDA to DDM on the optical transparency of the copolyimides. Since $([6FDA] + [PMDA])/[DDM] = 1.04$ for all cases, the molar ratio of 6FDA to DDM was inversely proportional to the molar ratio of PMDA to DDM. Therefore, an increase of $[6FDA]/[DDM]$ equivalently represents an increase of $[6FDA]/[PMDA]$.

domly distributed than in DDM-6FDA-PMDA and DDM-PMDA-6FDA copolyimide films, exhibited the highest contact angles or hydrophobicity, equivalently. Furthermore, the contact angle increased as the molar ratio of 6FDA to PMDA increased. Consequently, Figure 7 shows that DDM-(6FDA+PMDA) copolyimides had lower moisture contents than the other two series of copolyimides; and, the moisture content also decreased as the molar ratio of 6FDA to PMDA increased. These results could be attributed to the fluorine-containing moieties, such as $-C(CF_3)_2$ present in these polymers. The incorporation of hydrophobic $-C(CF_3)_2$ groups caused a decrease of the electronic density of the $-CO$ carbonyl groups, which are highly hydrophilic. In addition, the electronic density of the carbonyl groups would have been decreased more in the DDM-(6FDA+PMDA) copolyimides because the fluorine-containing moieties were more randomly bonded in the copolyimide backbones compared to the other two series.

Figure 8 shows the optical transparency of the copolyimide films. It increased as $[6FDA] : [PMDA]$ increased and the DDM-6FDA homopolyimide film indicated the highest optical transparency value of 76.6% because the $-C(CF_3)_2$ moieties could separate the chromophores and cut off the interactions between the electronic conjugates. Thus, the optical transparency of DDM-(6FDA+PMDA) copolyimide films was higher than those of the other two series, because the much randomly distributed $-C(CF_3)_2$

moieties in the DDM-(6FDA+PMDA) copolyimide backbones would separate the chromophores and cut off the electronic conjugate interactions more effectively than the other two series.

In the solubility test, it was found that all homopolyimides and copolyimides were insoluble in the common organic solvents, such as NMP and THF (tetrahydrofuran) as phase separation was clearly observed and the solid homopolyimide and copolyimide films were basically intact.

CONCLUSIONS

Two homopolyimides and three series of fluorine-containing copolyimides were prepared. The order of addition of the monomers as well as the molar ratio of 6FDA to PMDA affected the PA synthesis reactions. The PA solutions obtained from DDM-(6FDA+PMDA) showed the highest viscosities, and the viscosity decreased with the increase of the molar ratio of 6FDA to PMDA. The different series of copolyimide films obtained from different addition orders of the monomers contained different properties. The DDM-PMDA-6FDA copolyimides had the lowest dielectric constants. However, the DDM-(6FDA+PMDA) copolyimides indicated the highest contact angles, optical transparency, and the lowest moisture contents. The properties of these copolyimides also changed with the relative molar ratios of 6FDA and PMDA. All of the copolyimides exhibited excellent solvent resistance. TGA results showed that they all possessed excellent thermal stability and the onset temperature for decomposition decreased slightly as the molar ratio of 6FDA to PMDA increased.

REFERENCES

1. Satou, H.; Makino, D. in *Polymers for Electronic and Photonic Applications*; Wong, C. P., Ed.; Academic Press: New York, 1993, p 221.
2. Sasaki, S.; Nishi, S. In *Polyimides: Fundamentals and Applications*; Ghosh, M. K.; Mittal, K. L.; Eds.; Marcel Dekker: New York, 1996, p 71.
3. Mercer, F. W.; McKenzie, M. T.; Bruma, M.; Schulz, B. *Polym Int* 1994, 33, 399.
4. Bruma, M.; Sava, I.; Mercer, F.; Negulescu, I.; Daly, W.; Fitch, J.; Cassidy, P. *High Perf Polym* 1995, 7, 411.
5. Campbell, J. A.; Goodwin, A. A.; Mercer, F. W.; Reddy, V. *High Perf Polym* 1997, 9, 263.

6. Ando, S.; Matsuura, T.; Sasaki, S. *Macromolecules* 1992, 25, 5858.
7. Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules* 1992, 25, 3540.
8. Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. *Electronics Lett* 1993, 29, 269.
9. Hougham, G.; Tesoro, G.; Shaw, J. *Macromolecules*, 1994, 27, 3642.
10. Srinivas, S.; Graham, M.; Brink, M. H.; Gardner, S.; Davis, R. M.; McGrath, J. E.; Wilkes, G. L. *Polym Eng Sci* 1996, 36, 1928.
11. Rogers, M.E.; Brink, M. H.; McGrath, J. E.; Brennan, A. *Polymer* 1993, 34, 849.
12. Shiang, W. R.; Woo, E. P. *J Polym Sci Part A Polym Chem* 1993, 31, 2081.
13. Zoia, G.; Stern, S. A.; St. Clair, A. K.; Pratt, J. R. *J Polym Sci Part B Polym Phys* 1994, 33, 53.
14. Oishi, Y.; Itoya, K.; Kakimoto, M. K.; Imai, Y. *Polym J* 1989, 21, 771.
15. Iyoku, Y.; Kakimoto, M.; Imai, Y. *High Perf Polym* 1994, 6, 53.
16. Lee, D. S.; Quin, G. *Polym J* 1989, 21, 751.
17. Ree, M.; Yoon, D.Y.; Volksen, W. *J Polym Sci Part B Polym Phys* 1991, 29, 1203.
18. Rhee, S. B.; Park, J.-W.; Moon, B. S.; Chang, J. Y. *Macromolecules* 1993, 26, 404.
19. Kim, Y.; Ree, M.; Chang, T.; Ha, C. S.; Nunes, T. L.; Lin, J. S. *J Polym Sci Part B Polym Phys* 1995, 33, 2075.
20. Ree, M.; Kim, K.; Woo, S. H.; Chang, H. *J Appl Phys* 1997, 81, 698.
21. Han, H.; Seo, J.; Ree, M.; Pyo, S. M.; Gryte, C. C. *Polymer* 1998, 39, 2963.
22. Lee, C. J. In *Polymers for Electronic and Photonic Applications*; Wong, C. P., Ed.; Academic Press: New York, 1993, p 249.
23. Arnold, F. E.; Cheng, S. Z. D.; Hsu, S. L.-C.; Lee, C. J.; Harris, F. W.; Lau, S.-F. *Polymer* 1992, 33, 5179.
24. Bower, G. M.; Frost, I. W. *J Polym Sci Part A Polym Chem* 1963, 1, 3135.
25. Volksen, W.; Cotts, P. M. In *Polyimides: Synthesis, Characterization, and Applications*; Mittal, K. L., Ed.; Plenum Press: New York, 1984, Vol. 1, p 163.
26. Ohya, H.; Kudryavtsev, V. V.; Semenova, S. I. *Polyimide Membranes: Applications, Fabrications, and Properties*; Gordon and Breach: New York, 1996, p 52.