

Synthesis and Characterization of Fluorinated Polyimides for Optical Waveguide Application

Kwansoo Han

Applied Optics R&D Group, Samsung Electronics Co, Ltd., Suwon, P.O. Box 105, Kyungki-Do 440-600, Korea

Received May 17, 2000

Abstract : Fluorinated polyimides with high thermal stability, low optical absorption loss in the optical communication wavelengths of 1.3 and 1.55 μm , and low birefringence and water absorption have been investigated for optical waveguide applications. These polyimides were prepared from 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) with 1,4-bis-(4-amino-2-trifluoromethyl-phenoxy) tetrafluorobenzene (ATPT), 1,4-bis-(4-amino-2-trifluoromethyl-phenoxy) benzene (ATPB), and 1,3-bis-(4-amino-2-trifluoromethyl-phenoxy) 4,6-dichlorobenzene (ATPD), respectively. The polyimides obtained had glass transition temperatures that ranged from 260 to 280°C, and low water absorption less than 0.4% and low optical loss (> 0.2 dB/cm) at 1.3 and 1.55 μm . Birefringency values of polymer films ranged from 0.0041 to 0.0066.

Introduction

Polymeric materials are of great interest for applications in optical telecommunication such as optical waveguides and optical interconnections due to their ease of processing and relatively low cost compared to silica based materials.¹⁻³ To be used as optical polymers, low optical loss in the near-infrared wavelengths of 1.3 and 1.55 μm is the first consideration for optical telecommunication systems. Precise control of the refractive index and low birefringence are also important factors for fabricating optical waveguides. Finally, high thermal stability is required in order to provide compatibility with IC fabrication process.

It is known that the optical loss in polymeric materials at near-infrared (IR) wavelengths is mainly attributed to the absorption from vibrational overtones of carbon-hydrogen (C-H) bond, which can be reduced appreciably by the substitution of hydrogen atoms with deuterium, chlorine or fluorine.⁴⁻⁸ Thus, it is reported that fluorinated polymers are considered to be one of the potential candidates for optical applications because they

have excellent optical transparency at the optical telecommunication wavelengths.⁹⁻¹¹ Of the many polymers used as optical waveguides, fluorinated or perfluorinated polyimides find favor with a number of investigators due to their excellent thermal, mechanical, and optical properties.¹²⁻¹⁴ Films formed from polyimides, however, are frequently highly birefringent (the refractive index difference between in-plane and out-of-plane) due to their rigid structures. In highly birefringent materials, differently polarized lights would travel at different speeds. This would highly complicate the signal and cause polarization-dependent waveguide losses. Therefore, low birefringence of material is essential for the waveguide application.

In this paper, we describe the synthesis and characterization of a series of fluorinated polyimides which exhibit good thermal stability, low birefringence and water absorption, and low optical loss in the optical communication wavelengths of 1.3 and 1.55 μm for optical waveguide applications.

Experimental

Materials. Tetrafluoro-1,4-hydroquinone (Apollo Scientific), 2-chloro-5-nitrobenzotrifluoride (Aldrich),

*e-mail :hks@samsungchemical.co.kr

potassium carbonate (Aldrich), tetra-*n*-butyl ammonium chloride (Fluka), 10% Pd/C (Kojima Chem.) were used as received. Hydroquinone (Kanto Chem.) was recrystallized from toluene. 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, Chriskev) and 4,6-dichlororesorcinol (Aldrich) were purified by sublimation under reduced pressure prior to use. *N,N*-Dimethylacetamide (DMAc, Aldrich) was purified by distillation under reduced pressure over calcium hydride.

Monomer Synthesis. The monomers were prepared according to Scheme I.

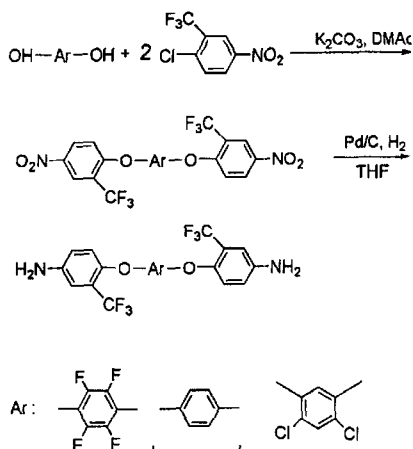
Bis-(4-nitro-2-trifluoromethyl-phenoxy) benzene Compounds (1a, 1b, and 1c): These compounds were synthesized similar to the one described by Wang.¹⁵ Tetrafluoro-1,4-hydroquinone (2.76 g, 0.015 mol), 6.91 g of potassium carbonate, and 40 mL of DMAc were placed under nitrogen in a 250 mL round-bottom flask. 2-Chloro-5-nitrobenzotrifluoride (7.52 g, 0.033 mol), 0.098 g of tetra-*n*-butyl ammonium chloride and 0.020 g of copper powder was then introduced into the reactor. The mixture was heated to 80°C for 17 hrs, and then filtered to remove copper powder. The filtered solution was precipitated in 500 mL of methanol-water (1:1 by volume). The resulting precipitate was collected by filtration and washed with 1.5 L of distilled water. After the precipitate was dissolved in tetrahydrofuran (THF), the solution was dried over magnesium sulfate. After removal of THF, the crude product (1a) was

purified by recrystallization from glacial acetic acid (m.p. 236°C). The yield was 5.51 g (65%). ¹H-NMR (acetone-*d*₆) δ 6.7-7.3 ppm (6H, aromatic). IR (KBr pellet) 1052 and 1234 cm⁻¹ (C-O-C), 1488 and 1333 cm⁻¹ (NO₂). Other two nitro compounds, 1,4-bis-(4-nitro-2-trifluoromethyl-phenoxy) benzene (yield; 72%) and 1,3-bis-(4-nitro-2-trifluoromethyl-phenoxy) 4,6-dichlorobenzene (yield; 63%) were obtained by a procedure similar to those mentioned above.

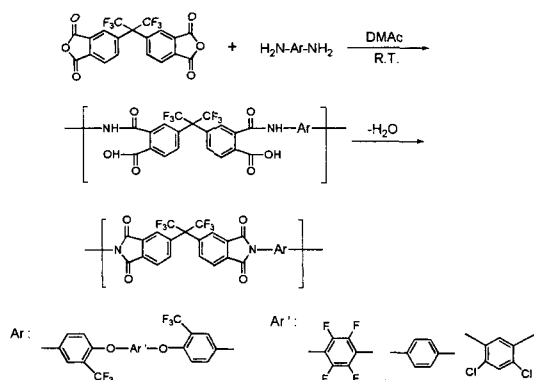
Bis-(4-amino-2-trifluoromethyl-phenoxy) benzene Compounds (2a, 2b, and 2c): 7 g of 1,4-bis-(4-nitro-2-trifluoromethyl-phenoxy) tetrafluorobenzene (1a), 0.7 g of 10% Pd/C and 60 mL of THF were introduced into one-neck round bottom flask. After the flask was evacuated, hydrogen gas was injected into the reaction mixture. Above procedure was repeated several times and the reaction mixture was stirred for 24 hrs at room temperature. Then the solution was filtered through celite to remove Pd/C. The filtered solution was poured into 200 mL of *n*-hexane to precipitate the white compound. It was dried at 50°C under reduced pressure to give 4.772 g of 2a (ATPT) (mp. 206°C, 76.3% yield). ¹H-NMR (acetone-*d*₆) δ 6.8-6.9 ppm (d, 2H, aromatic), δ 6.9-7.0 ppm (d, 2H, aromatic), δ 7.1-7.2 ppm (s, 2H, aromatic), and δ 4.9-5.0 ppm (s, 4H, NH₂). IR (KBr pellet) 1052 and 1260 cm⁻¹ (C-O-C), 3400 and 3490 cm⁻¹ (NH₂).

Other two amine compounds, 1,4-bis-(4-amino-2-trifluoromethyl-phenoxy) benzene (2b, ATPB) (mp. 180°C, yield; 75.5%) and 1,3-bis-(4-amino-2-trifluoromethyl-phenoxy) 4,6-dichlorobenzene (2c, ATPD) (mp. 153°C, yield; 52.6%) were obtained by a procedure similar to those mentioned above.

Polymerization and Film Preparation. Fluorinated polyimides were prepared according to general reaction as shown in Scheme II. Polymerizations were carried out under nitrogen atmosphere by adding stoichiometric amount of diamine and dianhydride in DMAc at room temperature. The resulting poly(amic acid) solutions were filtered through 1.0 μm Teflon filter and then spun coated on silicon wafer, followed by curing at 80°C/2 hrs, 160°C/1 hr, 250°C/0.5 hr, 300°C/0.5 hr, and 350°C/0.5 hr. Chemical imidization was also



Scheme I. Synthesis of fluorinated diamine monomers.



Scheme III. Synthesis of fluorinated polyimides.

carried out by adding acetic anhydride and pyridine ([acetic anhydride]/[pyridine] = 2 by volume) into poly(amic acid) solutions at room temperature for 48 hrs. The resulting polyimides were precipitated in water and then dried at 100°C under vacuum.

Measurements. A Varian Gemini 200 was used for $^1\text{H-NMR}$ measurements. Perkin Elmer DSC Pyris 1 was used to obtain the glass transition temperatures (T_g) of the polymers at a heating rate of 20°C/min. Thermogravimetric analyses (TGA) were carried on a Du Pont TGA 2950 thermal analyzer at a 10°C/min of heating rate in a nitrogen atmosphere. IR spectra of the synthesized monomers in KBr pallet were recorded by a ATI Mattson Infinity FTIR Spectrometer. Wide-angle X-ray diffraction patterns were performed with polymer films on a Philips PW 1710 X-ray diffractometer using Ni filtered $\text{Cu-K}\alpha$ radiation. Refractive indices of the polymer films were measured using Metricon 2010 prism coupler using light from a 1.55 μm laser diode. The inherent viscosities of poly(amic acid) samples were measured with an Ubbelohde viscometer using DMAc as a solvent. Near infrared spectra of the polyimide films (180- μm -thick) were recorded on an ATI Mattson Infinity FTIR Spectrometer. The absorption loss of polymer was calculated by using the equation described by Yoon.⁴ The water absorption was determined by immersing polyimide films in 25°C water. The weight differences after 3 days were measured.

Results and Discussions

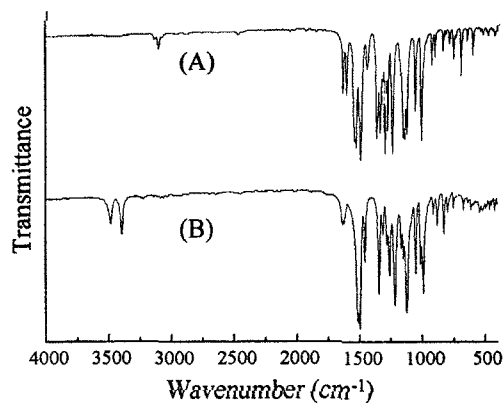


Figure 1. IR spectra of dinitro compound (1a), 1,4-bis-(4-nitro-2-trifluoromethyl-phenoxy) tetrafluorobenzene (A), and diamine compound (2a), 1,4-bis-(4-amino-2-trifluoromethyl-phenoxy) tetrafluorobenzene (ATPT) (B).

Synthesis of Monomers. The diamines, ATPT, ATPB, and ATPD, were synthesized in two steps by reaction of 2-chloro-5-nitrobenzotrifluoride with tetrafluoro-1,4-hydroquinone, hydroquinone, and 4,6-dichlororesorcinol, respectively, followed by reduction of nitro group with hydrogen in the presence of Pd/C as shown in Scheme I. The structures of the nitro and diamine compounds were confirmed by $^1\text{H-NMR}$ and IR. After reduction, the characteristic absorption peaks from at 1333 and 1488 cm^{-1} due to symmetric and asymmetric stretching of nitro group were disappeared, and absorption peaks from the amino group at 3400 and 3490 cm^{-1} due to N-H stretching were observed in IR spectra as shown in Figure 1. In $^1\text{H-NMR}$ spectra, the amino group signal around 4.95 ppm was observed after reduction.

Preparation of Polymers and Their Physical Properties. Fluorinated polyimides were synthesized from the reaction of 6FDA with ATPT, ATPB, and ATPD, respectively as shown in Scheme II. The intrinsic viscosities of resulting poly(amic acid)s were between 1.7 and 2.0 dL/g measured at 30°C in DMAc, exhibiting high molecular weight of these polymers. The measured glass transition temperatures of these polyimides are shown in Table I. As shown in this table, T_g increases in the order of 6FDA/ATPT > 6FDA/ATPD > 6FDA/ATPB. It seems that halogen substituents cause the decrease of the flexibility of the polymer chain (prevent rotation along the

Table I. Thermal Properties of the Polymers

Polymer	T_g (°C) ^a	Temperature of 5% Weight Loss (°C) ^b
6FDA/ATPT	278	517
6FDA/ATPB	260	524
6FDA/ATPD	270	490

^aDetermined by DSC at a heating rate of 20 °C/min in a nitrogen atmosphere.

^bDetermined by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

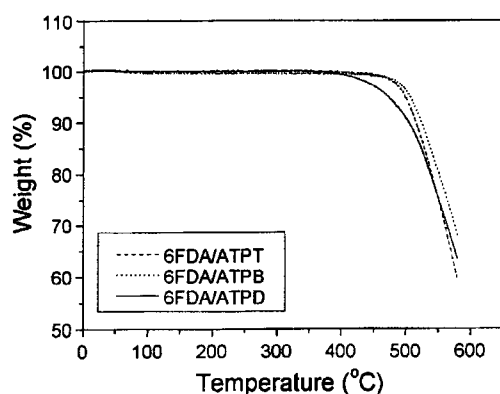


Figure 2. TGA thermograms of polyimides at a heating rate of 10 °C/min in a nitrogen atmosphere.

chain), and the increase of intermolecular interaction due to the increasing polarity of the polymer backbone. The thermal decomposition behaviors of polyimides are shown in Figure 2. It is observed that the decomposition starts at a lower temperature by halogen substitution. These temperatures decrease in the order of 6FDA/ATPB > 6FDA/ATPT > 6FDA/ATPD. This order correlates well with the order of bond dissociation energies of carbon-halogen (C-X) bonds.¹⁶

The solubility of the polyimides obtained by chemical imidization was tested in various solvents. Each polymer was immersed in six different solvents to determine its solubility. The polymers were considered slightly soluble if they dissolved at room temperature at concentrations below 10% (w/v) and soluble if they dissolved at concentrations of over 10%. All of polyimides were soluble in *m*-cresol, *N*-methyl-2-pyrrolidinone (NMP), DMAc, *N,N*-dimethylformamide (DMF), and cyclohexanone. The excellent solubility of these polyimides compared to conventional aromatic polyimides is

due partially to flexible linkages, the hexafluoroisopropylidene in 6FDA and the ether linkages in ATPT, ATPB, and ATPD. The increased solubility can also be attributed to the bulky-CF₃ group and halogen substituents (F or Cl) in diamines which prevented chain packing. The decrease in chain packing leads to an increase in free volume, which allows small solvent molecules to penetrate the polymer chain.^{17,18}

Crystallinity of the polymers was examined by the wide-angle X-ray diffraction diagram since prepared polymers are designed for optical waveguide applications. To be used as optical polymers, polymers should be amorphous. Otherwise, there is scattering loss due to the ordered structure. As shown in Figure 3, all the polyimides were amorphous. These results could be explained by the presence of flexible hexafluoroisopropylidene and ether groups, which prevent close packing of the polymer chains.¹⁹

The relationship between water absorption and fluorine content in the polyimides is shown in Table II. As shown in this table, water absorption decreases with increasing fluorine content. This phenomenon may be attributed to the hydropho-

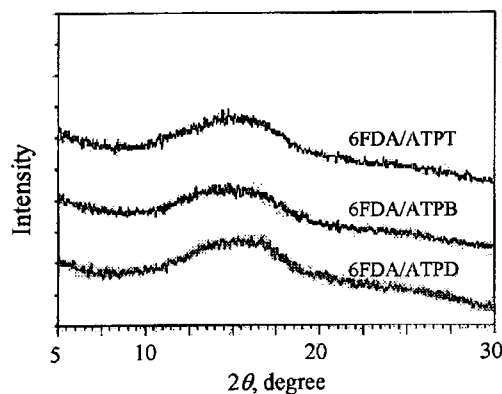


Figure 3. Wide-angle X-ray diffractograms of the polyimides.

Table II. Water Absorption of Polyimide Films

Polyimides	Water Absorption (%) ^a	Fluorine Content (%)
6FDA/ATPT	0.20	33.5
6FDA/ATPB	0.37	27.3
6FDA/ATPD	0.41	25.2

^aMeasured after 3 days.

bic effect of fluorine atoms. Low water absorption is essential for the low loss optical waveguides because absorbed water can cause absorption loss at the wavelength of 1.3 and 1.55 μm due to O-H absorption peak, and also change the refractive index. The water absorption of prepared polyimides is less than 0.4% due to high fluorine content, which is much less than that of nonfluorinated polyimides ($\sim 2\%$).²⁰

Optical Properties.

Optical Transparency in the Near Infrared (NIR) Region : Whereas the electronic transition causes the absorption in the UV and visible regions, the harmonics and their coupling of the stretching vibration of chemical bonds cause the absorption in the near-infrared region. Carbon-hydrogen (C-H) and oxygen-hydrogen (O-H) bond are reported to strongly affect the absorption in the near-infrared region.²¹ The low absorption in both 1.3 and 1.55 μm wavelengths, which are used in optical communications, is an important consideration in using these polymers for optical devices. It is reported that the absorption due to C-H bonds can be reduced by the replacement of hydrogen in C-H bonds to heavier atoms such as fluorine (F), chlorine (Cl) and deuterium (D).^{22,23} The absorption in the near-infrared region, therefore, is strongly related to the number of C-H bonds in the polymer. The smaller the number of C-H bonds in the polymer, the lower the absorption in the near-infrared region. Figure 4 shows the optical losses of 6FDA/ATPT film (180- μm -thick), which were calculated by using the equation described by Yoon.⁴ As shown in this figure, this polymer has very low optical absorption loss (> 0.2 dB/cm) at the telecommunication wave-

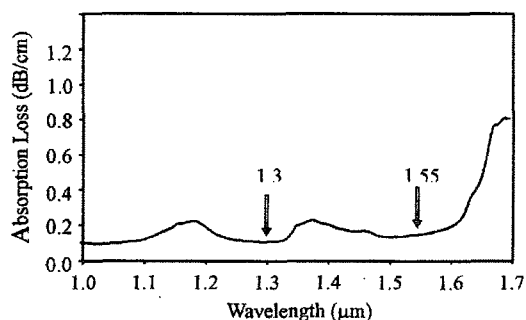


Figure 4. Absorption loss of 6FDA/ATPT.

lengths of 1.3 and 1.5 μm . The other polyimides, 6FDA/ATPD and 6FDA/ATPB, exhibited similar absorption behavior. Therefore, these polyimides are expected to be applicable to optical waveguide applications.

Refractive Index and Birefringence : The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, and birefringence (the difference between n_{TE} and n_{TM}) of the films were determined with a prism coupler.²⁴ In this method, laser light (1.55 μm) is passed through a polarizer and then into the face of the prism as shown in Figure 5. The beam refracts in the prism and travels toward the interface between the prism and the sample. Refractive indices of samples were determined by measuring the intensity change at various angles.

It is known that the refractive indices, and therefore, birefringence in polymer films are affected by several factors.²⁵ These factors include chain flexibility and linearity, the geometry of the repeat units, and the polarizability and orientation of the bonds in polymer backbone. As shown in Table III, the n_{TE} is larger than n_{TM} in every case. This is due to the rigid aromatic molecules, which tend to align in parallel with the film surface during the film processing. Due to this ordering, light travels slower (higher refractive index) in the in-plane direction compared with the out-of-plane direction. The n_{TE} 's and n_{TM} 's of films tend to increase in

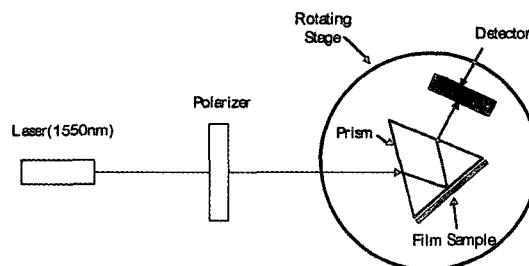


Figure 5. Diagram of the prism coupling apparatus.

Table III. Refractive Indices of Polyimide Films

Polyimides	n_{TE}^a	n_{TM}^a	Birefringence ($n_{TE} - n_{TM}$)
6FDA/ATPT	1.5089	1.5024	0.0065
6FDA/ATPB	1.5289	1.5224	0.0065
6FDA/ATPD	1.5344	1.5303	0.0041

^aDetermined by Metricon 2010 prism coupler using a 1.55 μm laser diode.

the order of 6FDA/ATPD > 6FDA/ATPB > 6FDA/ATPT, which is consistent with the increasing order of polarizability.

It is also known that the refractive indices of fluorine containing polymers are smaller than those of unfluorinated polymers due to the smaller polarizability of carbon-fluorine bond (C-F) compared to that of carbon-hydrogen (C-H) bond.²⁶ Because polarizability of carbon-chlorine (C-Cl) is larger than that of C-H bond, and light travels slower through more polarizable bonds, refractive index of chlorine containing polymer, 6FDA/ATPD, is the largest among the polymers. The birefringence of polyimides is in the range from 0.0041 to 0.0065. It is noted that the birefringence of 6FDA/ATPD is the smallest among the polymer. This is attributed to the kink structure of this polymer, and this structure prevents in-plane orientation. All these values are less than that of fluorinated polyimides based on 4,4'-(hexafluoroisopropylidene)diphthalic anhydride/2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (6FDA/TFDB) and 4,4'-oxydianiline (6FDA/ODA), which were used to fabricate optical waveguides (~0.008).^{27,28} These smaller birefringences are attributed to the flexible hexafluoroisopropylidene and oxygen bridging linkage, and bulky CF₃ groups in the polymers, which prevented in-plane orientation. This small birefringence is essential for the low loss optical waveguides because large birefringence can cause the polarization dependent loss (PDL).²⁶

In conclusion, fluorinated polyimides with good thermal stability, low birefringence and low water absorption, and low optical loss at the optical telecommunication wavelengths of 1.3 and 1.55 μm were synthesized. These polyimides had glass transition temperatures between 260-280°C and thermal decomposition temperatures at about 500°C. Because these polyimides had high fluorine contents, the polymers exhibited low water absorption, and optical loss at the optical communication wavelengths. These polymers also had very low birefringence owing to flexible hexafluoroisopropylidene and ether bridging linkage, and bulky CF₃ groups in the polymers. Therefore, the present polyimides can be considered as low loss optical polymeric materials for optical waveguide

applications.

References

- (1) N. Bouadma, J. Liang, R. Levenson, S. Grosmaire P. Boulet, and S. Sainson, *IEEE Photon. Lett.*, **6**, 1188 (1994).
- (2) T. Knoche, L. Muller, R. Klein, and A. Neyer, *Electron. Lett.*, **32**, 1284 (1996).
- (3) T. Matsuura, J. Kobayashi, S. Ando, T. Maruno, S. Sasaki, and F. Yamamoto, *Appl. Opt.*, **38**, 966 (1999).
- (4) I. McCulloch and H. Yoon, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 1177 (1995).
- (5) B. Boutevin, A. Rousseau, and D. Bosc, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1279 (1992).
- (6) K. Han, W. H. Jang, and T. H. Rhee, *Mol. Cryst. Liq. Cryst.*, **316**, 87 (1998).
- (7) K. Han, D. H. Suh, and T. H. Rhee, *Polym. Bull.*, **41**, 455 (1998).
- (8) K. Han, H. J. Lee, and T. H. Rhee, *J. Appl. Polym. Sci.*, **74**, 107 (1999).
- (9) H. J. Lee, E. M. Lee, M. H. Lee, M. C. Oh, J. H. Ahn, S. G. Han, and H. G. Kim, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 2881 (1998).
- (10) R. Yoshimura, M. Hikita, S. Tomaru, and S. Imamura, *J. Lightwave Technol.*, **16**, 1030 (1998).
- (11) C. Pitois, S. Vukmirovic, A. Hult, D. Wiesmann and M. Robertsson, *Macromolecules*, **32**, 2903 (1999).
- (12) T. Watanabe, N. Ooba, S. Hayashida, T. Kurihara and S. Imamura, *J. Lightwave Technol.*, **16**, 1049 (1998).
- (13) T. Matsuura, M. Ishizawa, Y. Hasuda, and S. Nishi *Macromolecules*, **25**, 3540 (1992).
- (14) T. Matsuura, N. Yamada, S. Nishi, and Y. Hasuda *Macromolecules*, **26**, 419 (1993).
- (15) C. S. Wang and R. W. Yang, *J. Appl. Polym. Sci.*, **66**, 609 (1997).
- (16) M. Nagata, N. Tsutsumi, and T. Kiyotsukuri, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 235 (1988).
- (17) D. J. Liaw and B. Y. Liaw, *Polymer J.*, **28**, 970 (1996).
- (18) D. J. Liaw and K. L. Wang, *J. Polym. Sci., Polym. Chem. Ed.*, **34**, 1209 (1996).
- (19) S. H. Hsiao, C. P. Yang, and C. K. Lin, *J. Polym. Res.*, **2**, 1 (1995).
- (20) T. Matsuura, *J. Photopolym. Sci. Technol.*, **10**, 31 (1997).
- (21) M. Usui, S. Imamura, S. Sugawara, S. Hayashida M. Sato, M. Hikita, and T. Izawa, *Electron. Lett.*, **30**, 958 (1994).
- (22) W. Groh, *Makromol. Chem.*, **189**, 2861 (1988).
- (23) T. Kaino, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 37 (1987).

Fluorinated Polyimides for Optical Waveguide

- (24) S. S Hardaker, S. Moghazy, C. Y. Cha, and R. J. Samuels, *J. Polym. Sci., Polym. Phys. Ed.*, **31**, 1951 (1993).
- (25) S. Herminghaus, D. Boese, D. Y. Yoon, and B. A. Smith, *Appl. Phys. Lett.*, **59**, 1043 (1991).
- (26) G. Hougham, Tesoro and Viehbeck, *Macromolecules*, **29**, 3453 (1996).
- (27) J. Kobayashi, T. Matsuura, S. Sasaki, and T. Maruno, *Appl. Opt.*, **37**, 1032 (1998).
- (28) J. Kobayashi, T. Matsuura, Y. Hida, S. Sasaki, and T. Maruno, *J. Lightwave Technol.*, **16**, 1024 (1998).