Perfluorinated Polyimide Synthesis

Shinji Ando,* **Tohru Matsuura, and**
Shigekuni Sasaki

NTT Interdisciplinary Research Laboratories,
Midori-cho 3-9-11, Musashino-shi, Tokyo 180, Japan

Polymers are expected to be used as media for transmitting near-infrared light in such optical communication applications as the waveguide in optoelectronic integrated circuits (OEIC) and in multichip interconnections.[1,2] The current manufacturing process for ICs and multichip modules includes soldering at 260 °C and short-term processes at temperatures of up to 400 °C. Waveguide polymeric materials should therefore have high thermal stability—that is, a high glass transition temperature (T_g) and a high polymer decomposition temperature—as well as high transparency at the wavelengths of optical communication (WOC), 1.0–1.7 μm.

Conventional waveguide polymeric materials, such as poly(methyl methacrylate) (PMMA) or polycarbonates (PC), do not have such thermal stability. In addition, their optical losses at the WOC are much higher than in the visible region (0.4–0.8 μm) because carbon–hydrogen bonds (C–H bonds) harmonically absorb near-infrared radiation. Two or more types of C–H bonds in PMMA and PC—those in methyl, methylene, methyne, and phenyl groups—give strong and multiple absorption peaks at the WOC. Conventional thermally stable polymers like polyimides, on the other hand, have been investigated as optical waveguide materials.[3-5] It has been reported that optimally cured partially fluorinated polyimides can be used to decrease optical losses below 0.1 dB/cm at 0.63 μm.[5] As described below, however, partially fluorinated polyimides also have some absorption peaks that originate from the C–H bonds in their phenyl groups.

The substitution of hydrogen atoms by deuterium (D) or fluorine (F) decreases optical losses because the wavelengths of the fundamental stretching vibrations of C–D and C–F bonds are about 1.4 and 2.8 times larger than that of the C–H bond.[6,7] Low loss waveguides of less than 0.1 dB/cm at 1.3 μm have been fabricated using deuterated or fluorodeuterated PMMA.[8] Perdeuteration, however, seems inadequate for decreasing optical losses over the entire WOC because the third harmonics of the C–D bond stretching appearing around 1.5 μm[9] is not negligible. On the other hand, perfluorinated amorphous polymers, such as Cytop (Asahi Glass Co.), have been reported to have no absorption peaks between 1.0 and 2.5 μm.[10] The combination of low optical losses in the near-infrared region and high thermal stability has therefore to be attained by the perfluorination of polyimides. This study reports the first synthesis of a perfluorinated polyimide.

Because of the high electronegativity of fluorine, the substitution of fluorine for all the hydrogens of aromatic diamines (except for those in amino groups) considerably decreases the reactivity of diamines for acylation. The electron-donating properties, which determine the reactivity for acylation,[11,12] of five kinds of diamines (shown in Figure 1) were estimated from ^{15}N and ^{1}H NMR chemical shifts. Of these five diamines, tetrafluoro-*m*-phenylenediamine (4FMPD) showed the highest reactivity.[13] Then the only existing perfluorinated dianhydride,[14] 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic di-
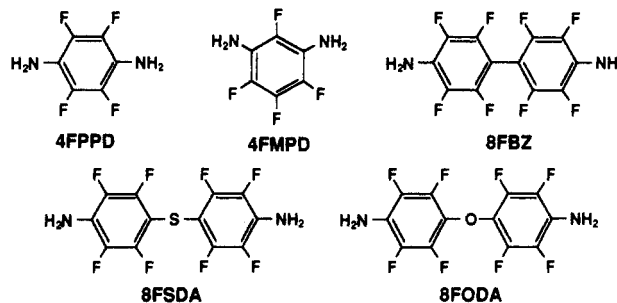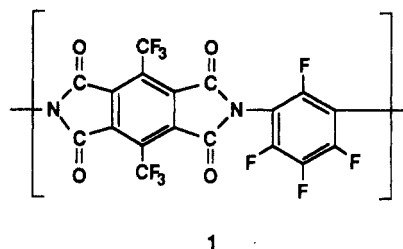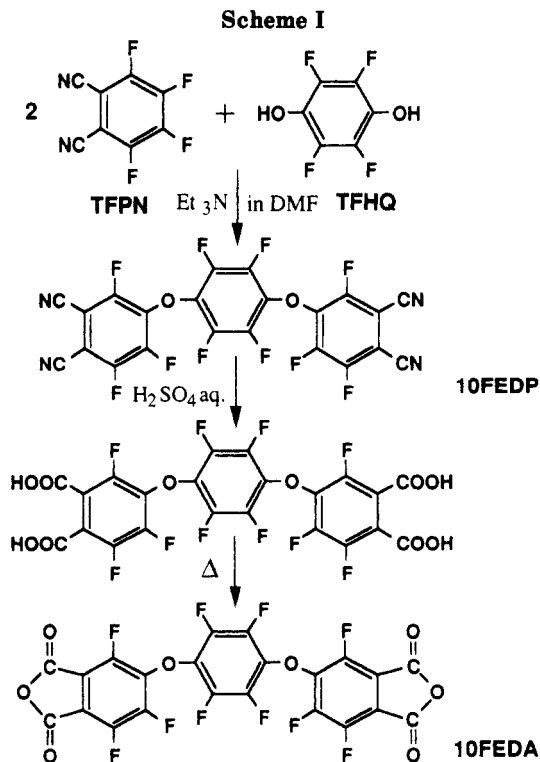

Figure 1. Structures of diamines.

anhydrides (P6FDA), was used to synthesize a perfluorinated polyimide with 4FMPD by the conventional two-step method (same as that described below). The perfluorinated polyimide (P6FDA/4FMPD, structure 1)

1

was, however, brittle and did not form a continuous film. This was due to the inflexibility of the polymer chain, which is ascribed to the absence of linkage groups between ring structures and to the steric interaction between fluorine and the trifluoromethyl group. Because the introduction of fluorine into dianhydrides, on the other hand, increases the reactivity for acylation,[12] tough and flexible films of perfluorinated polyimides are expected to be obtained by combining diamines, which have relatively high reactivities, with dianhydrides, which have flexible molecular structures.

A novel perfluorinated dianhydride, 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (10FEDA), was synthesized according to Scheme I. This
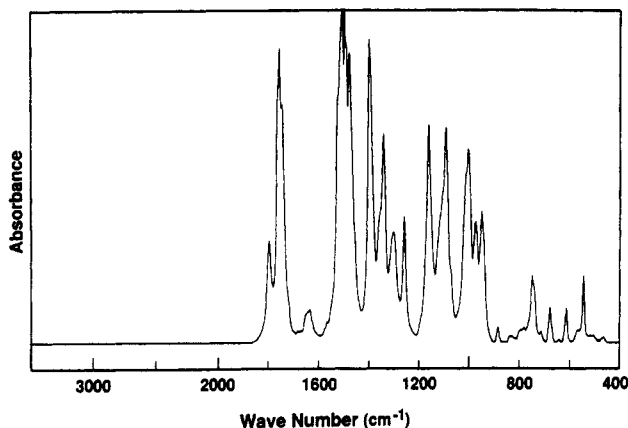
Scheme I

Figure 2. Infrared spectrum of a 10FEDA/4FMPD film.

Figure 3. TMA curve of a 10FEDA/4FMPD film.

Figure 4. ^{19}F NMR spectrum of 10FEDA/4FMPD dissolved in acetone-d_6 (the numbering of peaks corresponds to the fluorines in structure 2).

molecule has two ether linkages that give flexibility to the molecular structure. Tetrafluorophthalonitrile (TFPN) and tetrafluorohydroquinone (TFHQ) were stirred at room temperature, in the presence of triethylamine, in dimethylformamide (DMF). This reaction mixture was then poured into water, and the oily lower layer was extracted and washed again with water. This substance was recrystallized from methanol to afford 1,4-bis(3,4-dicyanotrifluorophenoxy)tetrafluorobenzene (10FEDP). The 10FEDP was then stirred in 80% sulfuric acid at 200 °C. After cooling the acid to room temperature, the precipitated white solid was filtered, quickly washed with water, and dried. The chemical shifts and signal ratios observed using ^{19}F NMR spectroscopy were consistent with the assigned structure. A dianhydride of 10FEDA thus obtained and a diamine of 4FMPD from Fuji Chemical Industries Ltd. were purified by sublimation under reduced pressure.

Equimolar amounts of 10FEDA and 4FMPD were added to N,N-dimethylacetamide (DMAc) to a concentration of 15 wt %, and the resulting solution was stirred at room temperature for 7 days under nitrogen. The solution of poly(amic acid) was spin-coated onto a silicon wafer and heated first at 70 °C for 2 h, then at 160 °C for 1 h, at 250 °C for 30 min, and finally at 350 °C for 1 h. The perfluorinated polyimide thus obtained (10FEDA/4FMPD, structure 2) was a tough and flexible film, pale yellow like

2
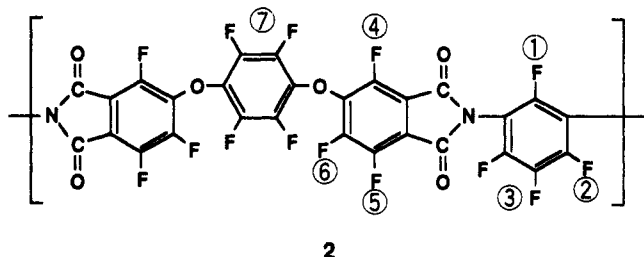
Kapton. This film was not soluble in polar organic solvents, such as N-methyl-2-pyrrolidinone (NMP), acetone, DMF, and DMAc. The infrared spectrum of the film (thickness 9.5 μm; Figure 2) had absorption peaks specific to imide groups (at 1755 and 1795 cm^{-1}) and no peaks due to C–H bonds (around 3000 cm^{-1}). This film, with a T_g of 309 °C measured by a thermal mechanical analyzer (TMA; Figure 3), has sufficient thermal stability above the soldering temperature. Thermal gravimetric analysis (TGA) showed the initial polymer decomposition temperature was 407 °C and 10% weight loss was at 501 °C. TMA and TGA measurements were conducted in nitrogen with heating rates of 5 and 10 °C/min, respec-
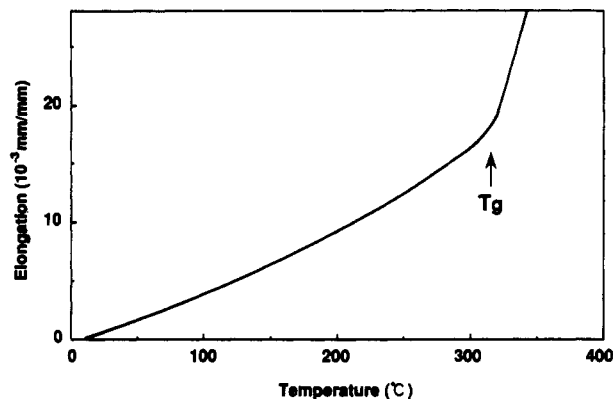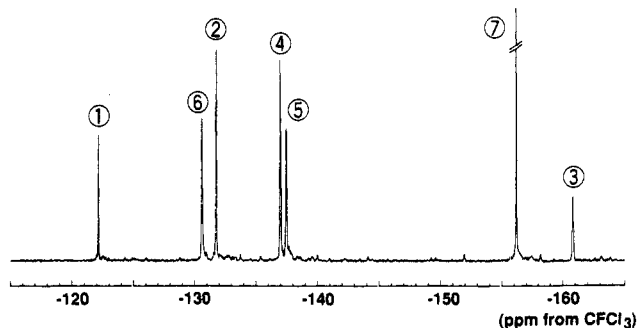
tively. The dielectric constant of the polyimide film was 2.8 at 1 kHz.

Furthermore, the 10FEDA/4FMPD film cured at 200 °C (stepwise at 70 °C for 2 h, at 160 °C for 1 h, and at 200 °C for 2 h) was soluble in such polar organic solvents. The ^{19}F NMR spectrum of 10FEDA/4FMPD dissolved in acetone-d_6 to a concentration of 5 wt % also confirmed the completion of imidization at 200 °C (Figure 4). The same phenomena have been observed for partially fluorinated polyimides.[15] The difference in solubility between the polyimides cured at 200 °C versus 350 °C may be explained by increased aggregation of the polyimide molecules with curing above T_g and/or by condensation of unreacted end groups of the polyimide. All the signals appearing in the spectrum were assigned, in which the numbering of peaks corresponds to the fluorines in structure 2. The visible–near-infrared absorption spectrum of the 10FEDA/4FMPD, cured at 200 °C and dissolved in acetone-d_6 to a concentration of 10 wt %, was measured with a 10-mm cell (Figure 5). The same amount of acetone-d_6 was used as a reference. A solid line indicates the absorbance of 10FEDA/4FMPD, and a dashed line indicates that of a partially fluorinated polyimide (6FDA/TFDB,[16] structure 3). Except for a small absorption peak

3
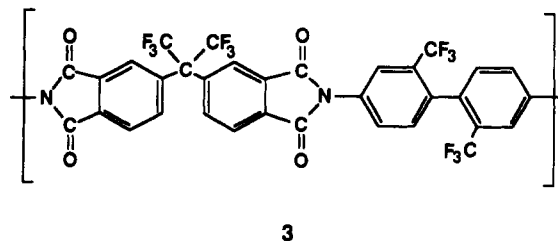
due to moisture absorbed in the solvent or adsorbed on the polyimide film ($\nu_{OH}(H_2O)$), the perfluorinated polyimide has no substantial absorption peaks over the entire
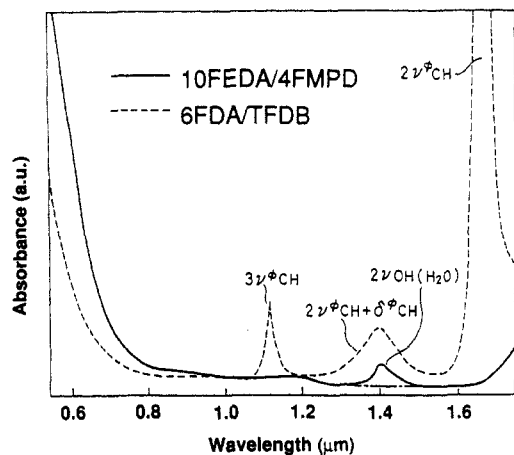
Figure 5. Visible–near-infrared absorption spectra of 10FEDA/4FMPD and 6FDA/TFDB dissolved in acetone-d_6.

WOC. Partially fluorinated polyimide, on the other hand, has an absorption peak due to the third harmonics of the stretching vibration of the C–H bond ($3\nu^\phi_{CH}$, 1.1 μm), a peak due to the combination of the second harmonics of the stretching vibration and the deformation vibration of the C–H bond ($2\nu^\phi_{CH} + \delta^\phi_{CH}$, 1.4 μm), and a peak due to the second harmonics of the stretching vibration of the C–H bond ($2\nu^\phi_{CH}$, 1.65 μm).

In conclusion, a perfluorinated polyimide that has T_g over 260 °C and a high optical transparency over the entire optical communication wavelengths was synthesized. Their high thermal stability and optical transparency are due to their fully aromatic molecular structure and the absence of C–H bonds. The use of a diamine, which has a relatively high reactivity, and a new perfluorinated dianhydride, which has a flexible structure, makes it possible to obtain a tough and flexible perfluorinated polyimide film. In addition, this polymer has a low dielectric constant. Perfluorinated polyimides are promising for use as optoelectronic materials.

References and Notes

(1) Schriever, R.; Franke, H.; Festl, H. G.; Kratzig, E. *Polymer* 1985, *26*, 1426.
(2) Kurokawa, T.; Takato, N.; Katayama, T. *Appl. Opt.* 1980, *19*, 3124.
(3) Franke, H.; Crow, J. D. *SPIE* 1986, *651*, 102.
(4) Sullivan, C. T. *SPIE* 1988, *994*, 92.
(5) Reuter, R.; Franke, H.; Feger, C. *Appl. Opt.* 1988, 27, 4565.
(6) Weeler, O. H. *Chem. Rev.* 1959, *59*, 629.
(7) Schleinitz, H. M. *Wire Cable Symp.* 1977, *25*, 352.
(8) Imamura, S.; Yoshimura, T.; Izawa, T. *Electron. Lett.* 1991, *27*, 1342.
(9) Kaino, T. *Appl. Phys. Lett.* 1986, *48*, 757.
(10) Aosaki, K. *Plastics (Jpn.)* 1991, *42*, 51.
(11) Okude, K.; Miwa, T.; Tochigi, K.; Shimanoki, H. *Polym. Prepr. (Am. Chem. Soc., Div. Chem. Soc.)* 1991, *32*, 61.
(12) Ando, S.; Matsuura, T.; Sasaki, S. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(13) Ando, S.; Matsuura, T.; Sasaki, S. *Polym. Prepr. Jpn.* 1991, *40*, 828.
(14) Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules* 1992, *25*, 3540.
(15) Ando, S.; Matsuura, T.; Sasaki, S. *Polymer* 1992, *33*, 2934.
(16) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* 1991, *24*, 5001.