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Polyimides Derived from 2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl. 2. Synthesis and Characterization of Polyimides Prepared from Fluorinated Benzenetetracarboxylic Dianhydrides

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ABSTRACT: A series of new fluorinated rigid-rod polyimides have been synthesized by the reaction of 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) with 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P6FDA), 1-(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P3FDA), or pyromellitic dianhydride (PMDA). The dielectric constant, refractive index, and water absorption decrease with an increasing number of trifluoromethyl side chains. The polyimide P6FDA/TFDB with the highest fluorine content prepared from TFDB and P6FDA has the lowest dielectric constant of 2.6 at 1 MHz, the lowest refractive index of 1.490 at 589.3 nm, and the lowest water absorption of 0.38%. On the other hand, the coefficient of thermal expansion (CTE) increases with an increasing number of trifluoromethyl side chains. The polyimide PMDA/TFDB prepared from TFDB and PMDA has a negative CTE of -5×10^{-6} °C^{-1} by thermomechanical analysis (TMA) and a high polymer decomposition temperature of 613 °C measured for a 10% weight loss in a nitrogen atmosphere by thermogravimetric analysis (TGA).

Introduction

We have already reported on the fluorinated polyimides derived from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) in a previous paper.[1] The polyimide prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) has a low dielectric constant, a low water absorption, a low refractive index, and a high optical transparency and is highly soluble in polar solvents due to the high fluorine content of 31.3%. On the other hand, the polyimide prepared from pyromellitic dianhydride (PMDA) has a relatively low fluorine content of 23.0% but shows a low coefficient of thermal expansion (CTE) on account of its rigid-rod structure.

Polyimides with a low dielectric constant, a low water absorption, and a low thermal expansion are very useful for interlayer dielectrics in electronic devices such as integrated circuits. Low dielectric constant polyimides and low water absorption polyimides were reported by Stoakley et al.[2] and Ruiz.[3] These properties have been observed in polyimides with trifluoromethyl groups introduced into the polymer backbone using 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and 6FDA monomers. The low thermal expansion polyimides were reported by Numata et al.[4] This property was observed in polyimides obtained from PMDA or 3,3′,4,4′-biphenyltetracarboxylic dianhydride and aromatic diamines which contained benzene rings only at the para positions. They proposed a relationship between the low CTE and the linearity in the polyimide molecular chains.

However, polyimides with all three properties (low dielectric constant, low water absorption, and low CTE) have not yet been made. Therefore, we have studied the synthesis of low thermal expansion fluorinated polyimides with a rigid-rod molecular structure. The rigid-rod polyimide main chain was based on 4,4′-diaminobiphenyl (benzidine) and PMDA. In practice, we used monomers of TFDB, which is benzidine with two trifluoromethyl groups, and 1-(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P3FDA) and 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P6FDA), which are PMDA with one and two trifluoromethyl groups, respectively.

Lukmanov et al. reported the synthesis of 1-(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic acid, the intermediate compound of P3FDA in detail.[5] Okuda et al. have estimated P3FDA polymerization reactivity using ^{1}H, ^{13}C, and ^{15}N NMR chemical shifts.[6]

This paper studies the synthesis of P6FDA and P3FDA monomers and the synthesis and characterization of polyimides based on TFDB diamine plus P6FDA, P3FDA, or PMDA dianhydride.

Experimental Section

Measurements. The IR spectra were measured with a Hitachi 270-30 IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker MSL-400 NMR spectrometer, using acetone-*d* or dimethyl-d_6 sulfoxide (DMSO-d_6) as a solvent. The chemical shifts were calibrated using tetramethylsilane (TMS). Mass spectra were measured with a Shimadzu QP-1000 quadrapole mass spectrometer equipped with a Shimadzu GC-9A gas chromatograph, using acetone as a solvent.

The intrinsic viscosities of the poly(amic acid)s in *N,N*-dimethylacetamide (DMAc) solutions were measured at 30 °C with a Ubbelohde viscometer set in a Lauda Viscotimer S.

The polymer decomposition temperatures were measured by thermogravimetric analysis (TGA) with a Shimadzu TGA-50 thermogravimetric analyzer. The TGA measurements were conducted with a heating rate of 10 °C/min in a nitrogen atmosphere.

The dielectric constants were measured with a YHP 4278 capacitance meter at a frequency of 1 MHz and a temperature of 23 °C. Dry samples were prepreconditioned of 1 Torr at 120 °C for 2 h to eliminate absorbed water. Wet samples were prepreconditioned to 50% relative humidity (RH) in an air atmosphere at 23 °C for 24 h after the measurement as dry samples.

The refractive indexes were measured with an Atago 4T-Type refractometer at 20 °C using light from the sodium D line with a wavelength of 589.3 nm.

The saturated water absorptions were measured by immersing the specimens in water at 23 °C. The weight differences before and after aging were measured.

The CTEs and grass transition temperatures (T_gs) were measured by thermomechanical analysis (TMA) with a Sinku Riko TMA-7000 thermomechanical analyzer. Specimen dimen-

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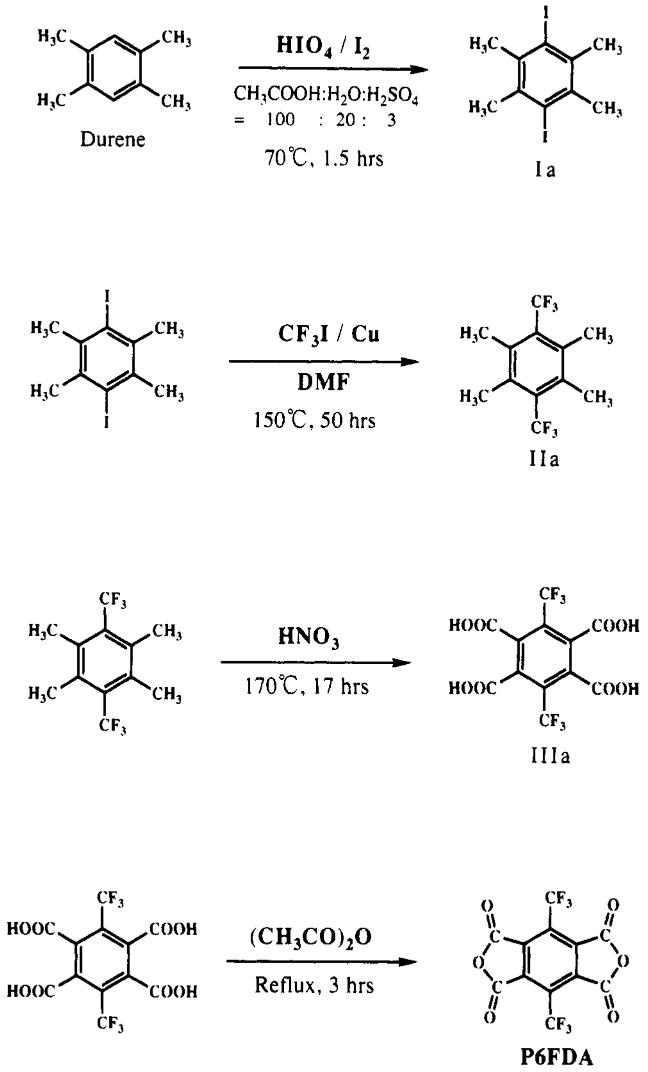
Scheme I



sions were 5 mm width, 15 mm long, and 15 μm thick. The measurements were carried out three times during elongation with a heating rate of 5 °C/min in a nitrogen atmosphere at a load of 3 g. After the first measurement (first run), the sample was cooled gradually to 25 °C in a nitrogen atmosphere. Then the second measurement (second run) was made. The same operation was carried out between the second run and the third measurement (third run). The CTE values were determined as the mean over the range 50–300 °C.

Monomer Synthesis. 1,4-Bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Dianhydride (P6FDA). P6FDA was synthesized in a four-step reaction (Scheme I).

Diiododurene (Ia). Starting from durene (from Tokyo Kasei Kogyo Co., Ltd.), diiododurene (**Ia**) was synthesized by the method given by Suzuki et al.[7]

1,4-Bis(trifluoromethyl)-2,3,5,6-tetramethylbenzene (IIa). In a 500-mL stainless steel autoclave, cooled iodotrifluoromethane (80 g, 0.408 mol, from PCR Inc.) was added to 280 mL of dimethylformamide (from Aldrich). Activated copper[8] (60 g) and Ia (60 g, 0.156 mol) were then also added. After the autoclave was purged with dry nitrogen at 50 atm, the mixture was stirred at 150 °C (80 atm) for 50 h. It was cooled, the pressure was reduced gradually, and the copper was removed by filtration. The solution was poured into excess water, and the precipitate was filtered off, washed with water, and dried. The product was purified by sublimation under reduced pressure to give 36 g (85% yield) of a white powder: mp 62.3–62.5 °C; MS (70 eV) *m/e* 270 (M^+); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.3 (q, $\mathrm{CH_3}$); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 125.4 (q, $\mathrm{CF_3}$), 130.3 (q, $\mathrm{C_{ar}CF_3}$), 135.1 (s, $\mathrm{C_{ar}CH_3}$), 17.3 (s, $\mathrm{CH_3}$).

1,4-Bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Acid (IIIa). In a 500-mL stainless steel autoclave, IIa (20 g, 0.075 mol) was added to 300 mL of 25% w/w nitric acid. After the autoclave was purged with dry nitrogen, the mixture was sealed and stirred at 170 °C for 17 h. It was cooled, and the precipitate was separated from the solution by filtration. This was dissolved in warm water and reprecipitated by adding hydrochloric acid. The white precipitate was filtered off and dried to give 22 g (75% yield) of the product: IR (KBr) 1700, 1760 (C=O), 3100 (OH) cm^{-1}, ^{1}H NMR (acetone-d_6, 400 MHz) δ 11.0 (s, COOH); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 122.0 (q, $\mathrm{CF_3}$), 126.9 (q, $\mathrm{C_{ar}CF_3}$), 134.6 (s, $\mathrm{C_{ar}COOH}$), 165.7 (s, COOH).

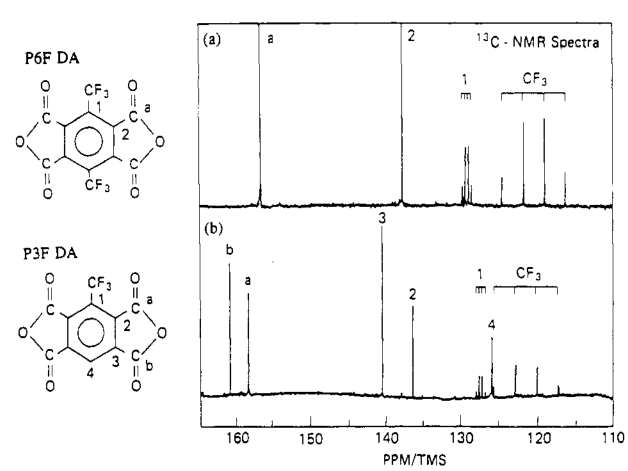


Figure 1. ^{13}C NMR spectra of P6FDA (a) and P3FDA (b).

1,4-Bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Dianhydride (P6FDA). In a 100-mL flask fitted with a condenser, IIIa (20 g, 0.05 mol) was added to acetic anhydride (40 g, 0.39 mol). The mixture was refluxed for 3 h. After it was cooled to room temperature, the white precipitate was filtered off, washed with ethanol, and dried at 50 °C for 2 h. The product was purified by sublimation under reduced pressure to give 12 g (60% yield) of the pure product: mp 239–240 °C; IR (KBr) 1800, 1860 (C=O) cm^{-1}; ^{13}C NMR (acetone-d_6, 100.6 MHz) as shown in Figure 1a.

1-(Trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Dianhydride (P3FDA). P3FDA was synthesized in a three-step reaction starting from iododurene using the same synthesis method as IIa, IIIa, and P6FDA.

2,3,5,6-Tetramethylbenzotrifluoride (IIb). IIb was prepared in the same manner as IIa with 2,3,5,6-tetramethyliodobenzene (70 g, 0.36 mol, from Tokyo Kasei Kogyo Co., Ltd., GR) instead of Ia to give 37 g (80% yield) of a white powder: mp 37.1–37.4 °C;[5] MS (70 eV) *m/e* 202 (M^+); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.2, 2.3 (s, $\mathrm{CH_3}$), 7.2 (s, $\mathrm{C_{ar}H}$); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 126.4 (q, $\mathrm{CF_3}$), 126.9 (q, $\mathrm{C_{ar}CF_3}$), 133.0, 135.3 (s, $\mathrm{C_{ar}CH_3}$), 134.9 (s, $\mathrm{C_{ar}H}$), 16.3, 20.1 (q, $\mathrm{CH_3}$).

1-(Trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Acid (IIIb). IIIb was prepared in the same manner as IIIa, with IIb (16.4 g, 0.0812 mol) instead of IIa, and with 325 mL of 25% nitric acid to give 19 g (73% yield) of a white solid: IR (KBr) 1720, 1740 (C=O), 3100 (OH) cm^{-1}; ^{1}H NMR (acetone-d_6, 400 MHz) δ 10.5 (s, COOH), 7.5 (s, $\mathrm{C_{ar}H}$); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 121.2 (q, $\mathrm{CF_3}$), 123.8 (q, $\mathrm{C_{ar}CF_3}$), 132.4, 137.1 (s, $\mathrm{C_{ar}COOH}$), 129.1 (s, $\mathrm{C_{ar}H}$), 164.6, 166.0 (s, COOH).

1-(Trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Dianhydride (P3FDA). P3FDA was prepared in the same manner as P6FDA with IIIb (1.61 g, 0.05 mol) instead of IIIa to give 8.1 g (57% yield) of a white powder: mp 189–190 °C; IR (KBr) 1800, 1850 (C=O) cm^{-1}; ^{1}H NMR (acetone-d_6, 400 MHz) δ 9.00 (s, $\mathrm{C_{ar}H}$); ^{13}C NMR (acetone-d_6, 100.6 MHz) as shown in Figure 1b.

Other Materials. The diamines and dianhydrides for polyimide synthesis are shown in Figure 2. TFDB was synthesized by the method given by Maki and Inukai[9] and was purified carefully by sublimination under reduced pressure. PMDA was obtained from Mitsui Toatsu Chemical, Inc., and was purified by recrystallization from acetone. 2,2′-Dimethyl-4,4′-diaminobiphenyl (DMDB) was obtained from Wakayama Seika Co., Ltd., and was purified by distillation under reduced pressure. 4,4′-Diamino-*p*-terephenyl (DPTP) was obtained from Nippon Carrid Co., Ltd., and was purified by recrystallization from tetrahydrofuran. DMAc, which had a water content below 0.005%

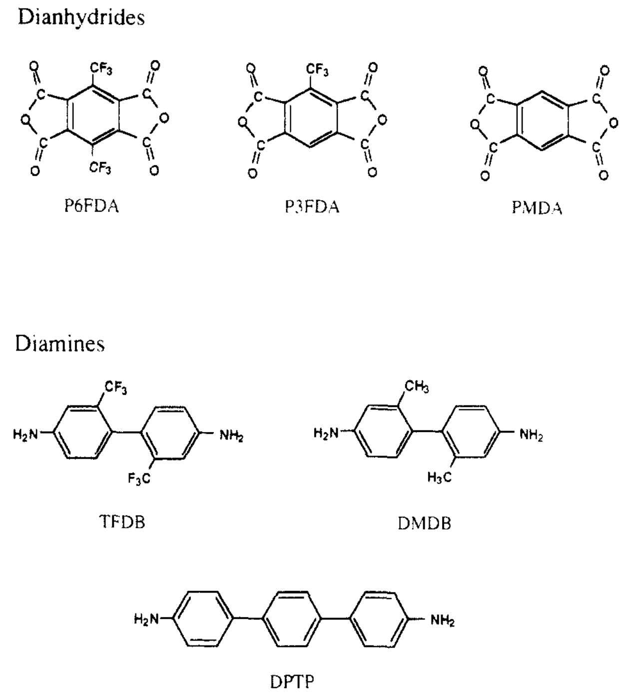
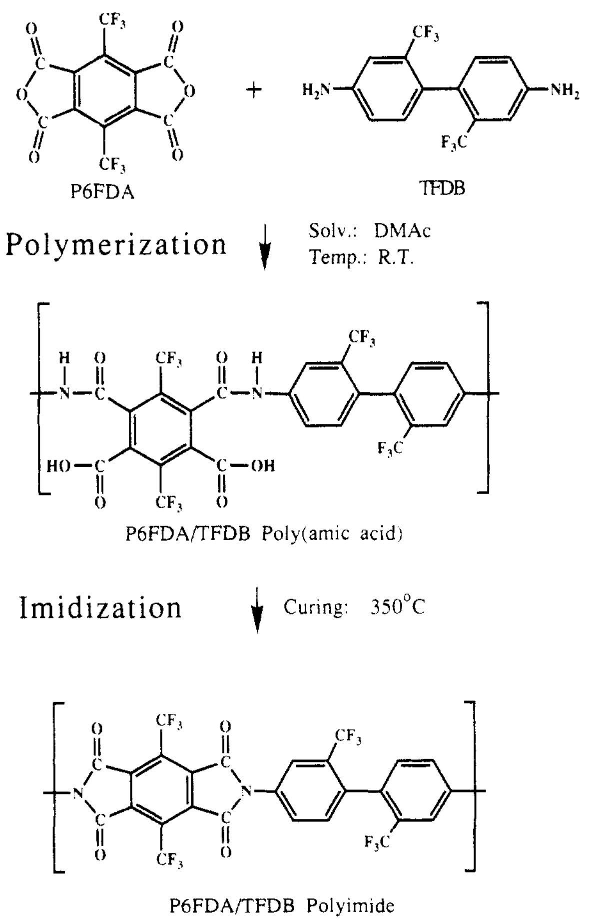


Figure 2. Chemical structures of dianhydrides and diamines.

Scheme II



and an evaporation residue below 0.0010%, was obtained from Aldrich and used without further purification.

Polyimide Preparation. The polyimide prepared from P6FDA and TFDB (P6FDA/TFDB). Preparation of the Poly(amic acid). The polyimide for this study was prepared by the reaction shown in Scheme II. P6FDA (5.3118 g, 15.000 mmol) was dissolved in DMAc (40.5 g) to give a clear, colorless solution. TFDB (4.8036 g, 15.000 mmol) was vigorously stirred into the solution. The solution was stirred in a dry nitrogen atmosphere at room temperature for 48 h. The solution became viscous. At this stage, 20% weight by poly(amic acid) solution was obtained (intrinsic viscosity 0.54 dL/g). This poly(amic acid) solution was frozen and kept at −50 °C in a dry nitrogen atmosphere to prevent decomposition. The entire preparation of poly(amic acid) was carried out in a dry nitrogen atmosphere.

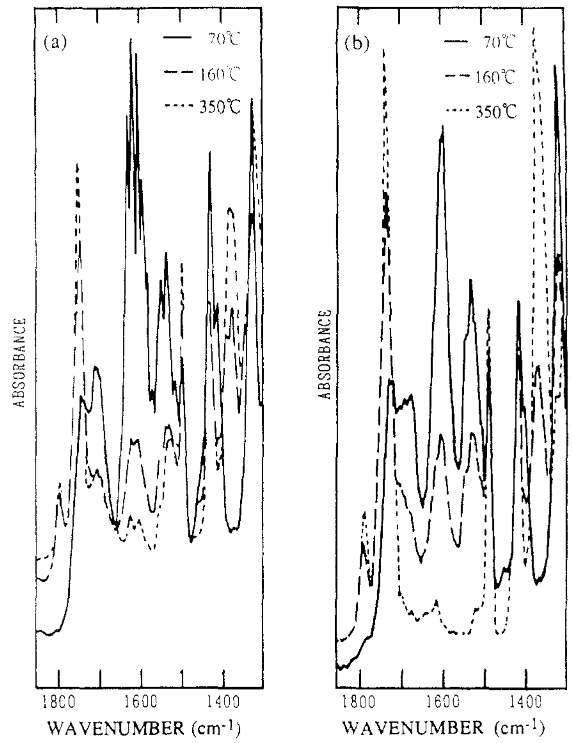


Figure 3. IR spectra of P6FDA/TFDB (a) and P3FDA/TFDB (b).

Conversion of Poly(amic acid) to Polyimide. The poly(amic acid) solution was spin-cast onto a clean dry silicon substrate to give a thin layer of solution. It was then heated to 350 °C in a dry nitrogen atmosphere in the following steps: 70 °C for 2 h, 160 °C for 1 h, 250 °C for 0.5 h, and 350 °C for 1 h. This heat treatment promoted imidization and converted poly(amic acid) into polyimide. The polyimide film was peeled from the silicon wafer. Films from 5 to 30 μm thick were obtained in this process. Whereas the IR absorption peak corresponding to carbonyl stretching of the amide group appeared at about 1720 cm^{-1} in the poly(amic acid), the absorption peaks corresponding to carbonyl asymmetric and symmetric stretching of imide groups appeared at 1740 and 1790 cm^{-1} in the polyimide (Figure 3a).

The polyimide prepared from P3FDA and TFDB (P3FDA/TFDB). P3FDA/TFDB poly(amic acid) solution (DMAc, 36.4 g, 20% by weight) was perpared in the same manner as P6FDA/TFDB but with P3FDA (4.2918 g, 15.000 mmol) instead of P6FDA and was then converted to P3FDA/TFDB polyimide in the same way as before. Whereas the IR absorption peak corresponding to carbonyl stretching of the amide group appeared at about 1720 cm^{-1} in the poly(amic acid), the absorption peaks corresponding to carbonyl asymmetric and symmetric stretching of imide groups appeared at 1740 and 1790 cm^{-1} in the polyimide (Figure 3b).

The other polyimides. PMDA/TFDB, P6FDA/DMDB, P3FDA/DMDB, PMDA/DMDB, P6FDA/DPTP, P3FDA/DPTP, and PMDA/DPTP poly(amic acid) solutions (DMAc, 10% or 20% by weight) were prepared in the same manner as P6FDA/TFDB and then converted into polyimides in the same way as before.

Results and Discussion

Synthesis of Fluorinated Dianhydrides. 1,4-Bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P6FDA). P6FDA was synthesized via the intermediate compounds Ia, IIa, and IIIa. The yield, melting point (mp), and elemental analysis data of all compounds are summarized in Table I.

Table I
Fluorinated Dianhydrides and Intermediate Compounds for Dianhydride Synthesis

compd	yield (%)	mp (°C)	elem anal. (calcd) (%) C	H	I	F
Ia	38	140–141	31.16 (31.12)	3.11 (3.13)	65.84 (65.75)	
IIa	85	62.3–62.5	53.44 (53.34)	4.45 (4.48)		41.93 (42.18)
IIIa	75		36.81 (36.94)	0.99 (1.03)		29.10 (29.22)
P6FDA	60	239–240	40.22 (40.70)	<0.1 (0)		31.58 (32.19)
IIb	80	37.1–37.4	65.19 (65.34)	6.42 (6.48)		28.27 (28.18)
IIIb	73		40.54 (41.01)	1.57 (1.56)		17.57 (17.69)
P3FDA	57	189–190	45.57 (46.18)	0.35 (0.35)		19.80 (19.92)

The reaction of durene with iodine in the presence of a periodic acid gave Ia. The melting point of Ia, 140–141 °C, agreed with that in the reference.[8] The peak (*m/e* 386) for Ia molecules was observed in the mass spectrum.

The reaction of Ia with iodotrifluoromethane in the presence of copper gave IIa.

The oxidation of IIa at 170 °C for 17 h gave IIIa. IIIa started to melt at 244 °C at atmospheric pressure. However, the melting point could not be determined, because IIIa easily converted into P6FDA (mp 239–240 °C) during heating.

The reaction of IIIa with acetic dianhydride gave P6FDA. The ^{13}C NMR spectrum is shown in Figure 1a.

1-(Trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Dianhydride (P3FDA). P3FDA was synthesized via the intermediate compounds IIb and IIIb. The yield, mp, and elemental analysis data of all compounds are summarized in Table I.

The reaction of iododurene with iodotrifluoromethane in the presence of copper gave IIb.

The oxidation of IIb at 170 °C for 17 h gave IIIb. At atmospheric pressure, IIIb melted at 247–248 °C, which is lower than in the reference, 280–281 °C,[5] because IIIb may be converted into P3FDA (mp 189–190 °C) while the mp is measured.

The reaction of IIIb with acetic anhydride gave P3FDA. The ^{13}C NMR spectrum is shown in Figure 1b.

Intrinsic Viscosity. Figure 4 shows the intrinsic viscosities of the poly(amic acid)s. The intrinsic viscosity of PMDA/TFDB is lower than that of PMDA/DMDB because the nucleophilicity of the amino group affects the polymerization reactivity. DMDB possesses amino groups with a high electron density owing to the electron-releasing methyl groups, but TFDB possesses amino groups with a lower electron density owing to the electron-attracting trifluoromethyl groups.

The intrinsic viscosity decreases with an increasing number of trifluoromethyl side chains in the dianhydride unit, either because it is easy to open the dianhydride ring by introducing trifluoromethyl groups and/or because chain–chain interaction decreases with increasing fluorine content.

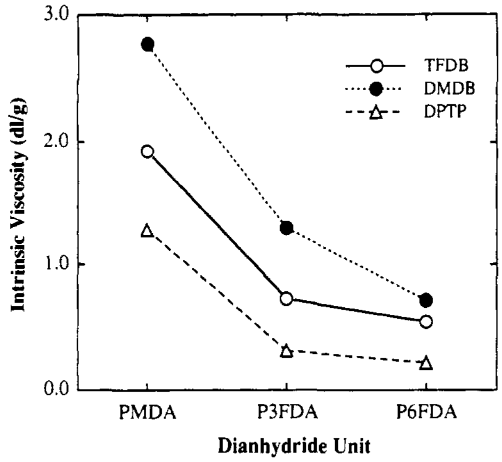


Figure 4. Intrinsic viscosity of fluorinated polyimides.

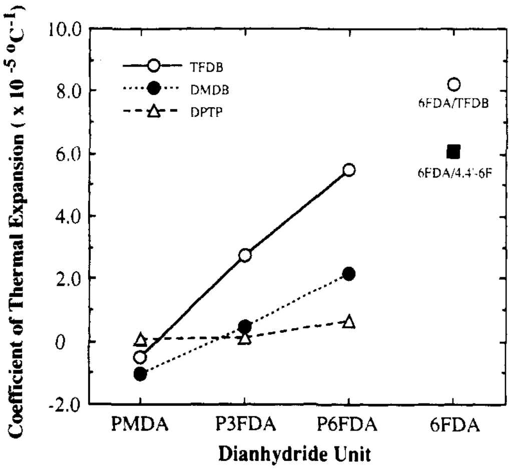


Figure 5. Coefficient of thermal expansion of fluorinated polyimides. Temperature range, 50–300 °C; second run.

Thermal Expansion Behavior. The CTEs (second run) of the polyimides are shown in Figure 5. In the third run of TMA measurement in all samples, the CTEs are almost the same as those of the second run. These polyimides exhibit lower CTEs than already known fluorinated polyimides such as 6FDA/4,4′-6F, prepared from 6FDA and 2,2-bis(4-aminophenyl)hexafluoropropane (4,4′-6F), and 6FDA/TFDB. In the polyimides prepared from the same diamines of TFDB, DMDB, or DPTP, the CTE increases as the number of trifluoromethyl side chains in the dianhydride unit increases. In the three polyimides prepared from the same dianhydride of P6FDA, P6FDA/TFDB with trifluoromethyl side chains in the diamine unit shows a higher CTE than P6FDA/DMDB with methyl side chains in the diamine unit. P6FDA/DPTP without side chains in the diamine unit shows the lowest CTE. In the three polyimides prepared from the same dianhydride of P3FDA, the same relationship between CTE and side chains as with P6FDA is obtained. These results suggest that side chains, such as methyl groups and trifluoromethyl groups, loosen the molecular packing, the trifluoromethyl side chain having a larger effect than the methyl side chain.

In the three polyimides prepared from the same dianhydride of PMDA, the relationship between the structure of the diamine unit and the CTE is different from those using P3FDA and P6FDA. PMDA/TFDB and PMDA/DMDB exhibit negative CTEs. There may be some ordering in the film plane caused by the process of spin-casting or curing.

Thermal Stability. Figure 6 shows the polymer decomposition temperatures of the polyimides. These results indicate that PMDA/DPTP having a high rigidity in the polyimide main chain and no side chains produced the highest polymer decomposition temperature. Among the polyimides prepared from each diamine, the polymer decomposition temperature increases as the number of trifluoromethyl chains in the dianhydride decreases. Among the polyimides prepared from PMDA, PMDA/

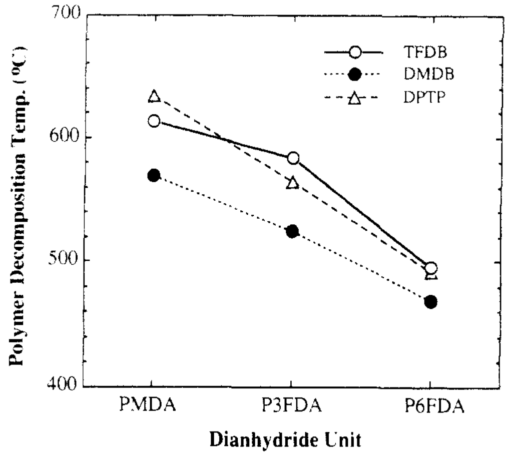


Figure 6. Polymer decomposition temperature of fluorinated polyimides. 10% by weight loss in a nitrogen atmosphere.

Table II
Glass Transition Temperatures of Polyimides

polymer	T_g (°C)
P6FDA/TFDB	304
P3FDA/TFDB	373
PMDA/TFDB	none detected
P6FDA/DMDB	385
P3FDA/DMDB	373
PMDA/DMDB	374
P6FDA/DPTP	364
P3FDA/DPTP	364
PMDA/DPTP	none detected

DPTP, without side chains in the diamine unit, has the highest polymer decomposition temperature. The polyimides prepared from TFDB have higher polymer decomposition temperatures than those from DMDB, regardless of the dianhydride unit structure. Side chains such as methyl groups and trifluoromethyl groups decompose more easily than the main chain which includes imide rings and aromatic rings. The binding energy of the C–F bond (105.4 kcal/mol) is larger than that of the C–H bond (98.8 kcal/mol). Therefore, the polyimides with methyl side chains have a lower polymer decomposition temperature.

Table II shows the T_gs of the polyimides. The T_gs of all polyimides are higher than 300 °C. In particular, PMDA/TFDB and PMDA/DPTP failed to exhibit T_gs below 400 °C using TMA measurement.

Dielectric Properties. Figure 7 shows the dielectric constants of the polyimides, PMDA/TFDB, P3FDA/TFDB and P6FDA/TFDB, which have similar molecular structures but different fluorinated substituents. The dielectric constant decreases with an increasing fluorine content. The lowest dielectric constant in the dry condition is 2.6 at 1 MHz for P6FDA/TFDB. The low dielectric constants of the fluorinated polyimides result from reduced chain–chain electronic interaction due to the low electronic polarizability of the fluorine.[10]

The dielectric constant of polyimide films in the wet condition (50% RH atmosphere) is higher than in the dry condition. This is attributed to water absorption by the polyimides. Figure 8 shows the water absorption of the polyimides. The water absorption decreases with an increasing fluorine content because of the hydrophobic effect of fluorine atoms. The water absorption is related to the stability of the dielectric constant. The dielectric constant of polyimides with a higher fluorine content, P3FDA/TFDB and P6FDA/TFDB, in the wet condition, is a littler larger than those in the dry condition (Figure 7). The dielectric constant variability of highly fluorinated polyimides is smaller than that of the polyimide with a low flourine content, PMDA/TFDB. In Figure 7, the dielectric constant difference between wet and dry conditions for P6FDA/TFDB is much greater than one would expected. P6FDA/TFDB has a lower intrinsic viscosity than both P3FDA/TFDB and PMDA/TFDB and has a larger hydrophilic effect due to the larger amount of end groups. These results indicate that introducing fluorine into the polyimide structure is effective for stabilizing the dielectric constant because of the low water absorption. The stability of the dielectric constant is important for interlayer dielectrics in microelectronic devices.

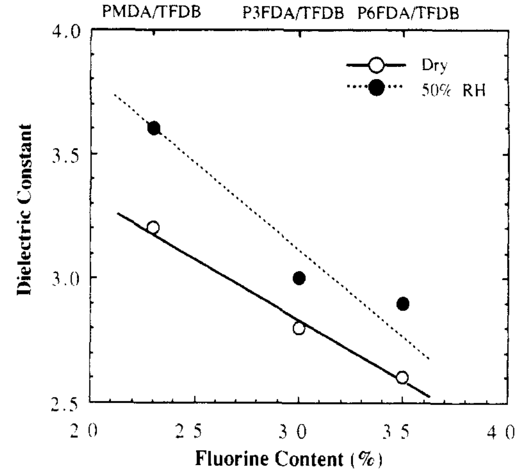


Figure 7. Dielectric constant of fluorinated polyimides. Frequency, 1 MHz.

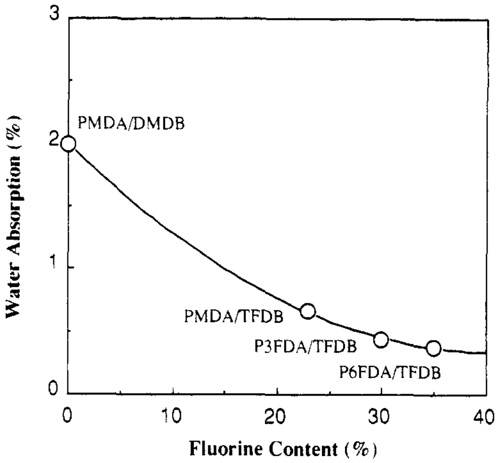


Figure 8. Water absorption of polyimides.

Optical Properties. The refractive indexes of polyimide films are shown in Figure 9. The refractive index decreases with increasing fluorine content. P6FDA/TFDB has the lowest refractive index because of its low electronic polarizability as well as its low dielectric constant.

After imidization by heating at 350 °C, the polyimide films are transparent and tough, except for the P6FDA/TFDB film, which is opaque. In P6FDA/TFDB, there may be not only imidization but also side reactions such as cross-linking and chain scission by heating, because of the strong electron affinity of the two trifluoromethyl groups in the dianhydride unit.

Conclusions

Two fluorinated dianhydrides for polyimides, P3FDA and P6FDA, have been synthesized. These dianhydrides and PMDA were polymerized to polyimides using TFDB, DMDB, and DPTP diamines. The relationship between structure and properties is summarized as follows:

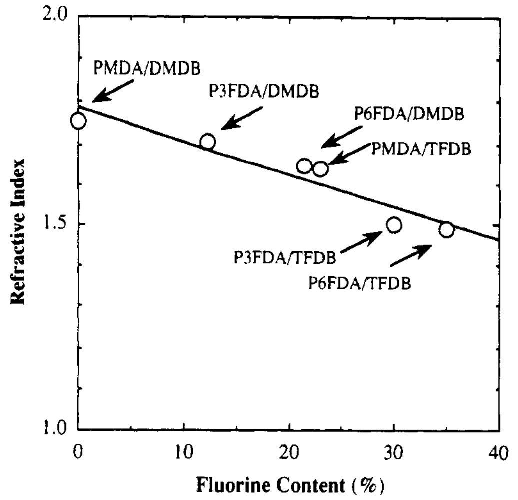


Figure 9. Refractive index of polyimides. Light wavelength, 589.3 nm; temperature, 20 °C.

(1) Introduction of trifluoromethyl side chains into dianhydride units increases the CTE but decreases the dielectric constant, the water absorption, the refractive index, the polymer decomposition temperature, and the intrinsic viscosity.

(2) Polyimides with trifluoromethyl side chains in the diamine unit have higher CTEs and polymer decomposition temperatures than those with methyl side chains. On the other hand, polyimides with trifluoromethyl side chains have lower intrinsic viscosities than those with methyl chains.

(3) The dielectric constant, the refractive index, and the water absorption decrease when the fluorine content is increased by introducing trifluoromethyl side chains into polyimide molecules.

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References and Notes

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Registry No. Ia, 3268-21-1; IIa, 97630-74-5; IIb, 3360-65-4; IIIa, 128298-23-7; IIIb, 53812-59-2; P6FDA, 128082-91-7; P3FDA, 114349-13-2; (TFDB)(P6FDA) (copolymer), 135572-33-7; (TFDB)(P6FDA) amic acid (SRU), 141319-24-6; (TFDB)(P6FDA) imide (SRU), 135364-55-5; (TFDB)(P3FDA) (copolymer), 129342-67-2; (TFDB)(P3FDA) amic acid (SRU), 138634-38-5; (TFDB)(P3FDA) imide (SRU), 135421-50-0; (TFDB)(PMDA) (copolymer), 129197-24-6; (TFDB)(PMDA) amic acid (SRU), 134904-53-3; (TFDB)(PMDA) imide (SRU), 129219-40-5; (P6FDA)(DMDB) (copolymer), 141223-63-4; (P6FDA)(DMDB) amic acid (SRU), 141319-25-7; (P6FDA)(DMDB) imide (SRU), 141223-65-6; (P3FDA)(DMDB) (copolymer), 141223-64-5; (P3FDA)(DMDB) amic acid (SRU), 141319-28-0; (P3FDA)(DMDB) imide (SRU), 141223-66-7; (PMDA)(DMDB) (copolymer), 117344-86-2; (PMDA)(DMDB) amic acid (SRU), 117312-35-3; (PMDA)(DMDB) imide (SRU), 117456-41-4; (P6FDA)(DPTP) (copolymer), 135572-39-3; (P6FDA)(DPTP) amic acid (SRU), 141319-27-9; (P6FDA)(DPTP) imide (SRU), 135364-59-9; (P3FDA)(DPTP) (copolymer), 135572-38-2; (P3FDA)(DPTP) amic acid (SRU), 135364-58-8; (P3FDA)(DPTP) imide (SRU), 135364-58-8; (PMDA)(DPTP) (copolymer), 55879-29-3; (PMDA)(DPTP) amic acid (SRU), 59494-81-4; (PMDA)(DPTP) imide (SRU), 55879-14-6; (6FDA)(4,4′-6F) (copolymer), 129197-26-8; (6FDA)(4,4′-6F) imide (SRU), 12919-40-5; CF_3I, 2314-97-8; 2,3,5,6-tetramethyliodobenzene, 2100-25-6.