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Color lightness and highly organosoluble fluorinated polyamides, polyimides and poly(amide–imide)s based on noncoplanar 2,2′-dimethyl-4,4′-biphenylene units

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Abstract

A new diamine monomer containing noncoplanar methyl substitution, 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-aminophenoxy)biphenyl (DBTFAPB) was successfully synthesized and used in the preparation of a series of polyamides and polyimides by direct polycondensation with various aromatic dicarboxylic acids and tertacarboxylic dianhydrides. A new noncoplanar dicarboxylic acid monomer containing noncoplanar methyl substitution, 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-trimellitimidophenoxy)biphenyl (DBTFTPB) was also successfully synthesized by refluxing the diamine, DBTFAPB, with trimellitic anhydride in glacial acetic acid. A series of new poly(amide–imide)s were prepared directly from DBTFTPB with various diamines in *N*-methyl-2-pyrrolidinone (NMP). All the polymers exhibited excellent solubility in solvents, such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine, tetrahydrofuran (THF), cyclohexanone and γ-butyrolactone at room temperature or upon heating at 70 °C. Inherent viscosities of the polymers were found to range between 0.60 and 1.34 dL g^{-1}. Gel permeation chromatography (GPC) of the polymers showed number-average and weight-average molecular weight up to 7.3×10^4 and 17.9×10^4, respectively. These polymers showed that the glass transition temperatures were between 230 and 265 °C, and the 10% mass loss temperatures were higher than 460 °C in nitrogen atmosphere. All the polymers could be cast into flexible and tough films from DMAc solutions. They had a tensile strength in the range of 82–124 MPa and a tensile modulus in the range of 1.9–2.9 GPa. These polymers exhibited low dielectric constants ranging from 2.87 to 4.03, low moisture absorption in the range of 0.29–3.20%, and high transparency with an ultraviolet–visible absorption cut-off wavelength in the 347–414 nm range.

Keywords: Noncoplanar; Dielectric constant; Birefringence

1. Introduction

Aromatic polyamides, polyimides and poly(amide–imide)s have been noted for their excellent characteristics such as thermal stability, electrical properties and chemical resistance as well as their high strength and high modulus as fibers [1,2]. However, the main drawbacks of these classes of aromatic polymers are their insolubility and high glass transition temperature that cause difficulties in both synthesis and processing [3,4]. Therefore, several approaches have been made through synthetic modification by the incorporation of flexible linkages [5,6], bulky pendant groups [7–9] and noncoplanar biphenylene moieties [10–12] into the polymer backbones.

The 2,2′-dimethyl biphenylene moiety could be considered as a rod-like structure. The substitution at the 2- and 2′-positions of the biphenyl moiety appears to force the two phenyl rings into adopting a noncoplanar conformation. This has resulted in disrupted crystal packing, enhanced solubility and optical transparency [11–15]. Recently, considerable attention has been devoted to the synthesis of fluorine-containing polymers. Incorporation of the bulky fluorine groups serves to increase the free volume of the polymers, thereby improving some properties like solubility, gas permeability [16], optical transparency [17,18] and flame resistance [19]. In addition, it also reduces the moisture absorption, crystallinity, dielectric constant and color.

In this study, we successfully prepared two novel monomers, 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-aminophenoxy)biphenyl (DBTFAPB) and 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-trimellitimidophenoxy)biphenyl

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(DBTFTPB), containing trifluoromethyl group as well as 2,2′-dimethyl biphenylene, and aryl–ether unit. Polyamide, polyimide and poly(amide–imide) were prepared from these monomers. The synthesis and properties of these polymers such as solubility, optical transparency, refractive index, thermal and mechanical properties, as well as dielectric constant and coefficient of thermal expansion are also investigated and discussed.

2. Experimental

2.1. Materials

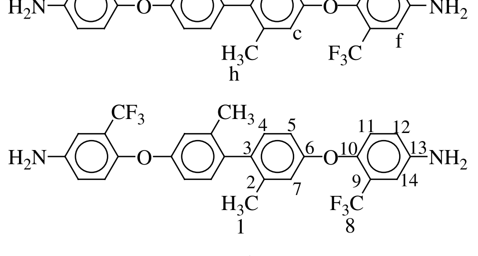
2,2′-Dimethyl-4,4′-diaminobiphenyl dihydrochloride (Wakayama Seika Co.), 2-chloro-5-nitrobenzotrifluoride (ACROS), anhydrous potassium carbonate (MERCK), hydrazine monohydrate (MERCK), and 10% palladium on activated carbon (MERCK) were used as received. Reagent-grade aromatic dicarboxylic acids such as isophthalic acid (I-1, Wako), 2,6-naphthalenedicarboxylic acid (I-2, TCI), 4,4′-biphenyldicarboxylic acid (I-3, TCI), 5-*tert*-butylisophthalic acid (I-4, Aldrich), 4,4′-sulfonyldibenzoic acid (I-5, New Japan Chemical Co.), terephthalic acid (I-6, Acros) and 4,4′-(hexafluoroisopropylidene)dibenzoic acid (I-7, Aldrich); and aromatic tetracarboxylic dianhydrides such as 4,4′-hexafluoroisopropylidenediphthalic anhydride (II-1, CHRISKEV), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (II-2, CHRISKEV), 4,4′-sulfonyldiphthalic anhydride (II-3, New Japan Chemical Co.), and 4,4′-oxydiphthalic anhydride (II-4, TCI) were recrystallized from acetic anhydride prior to use. Reagent-grade calcium chloride was dried under vacuum at 180 °C prior to use. Trimellitic anhydride (MERCK) was purified by sublimation. *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride before polymerization.

2.2. Synthesis of 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-nitrophenoxy)biphenyl (DBTFNPB)

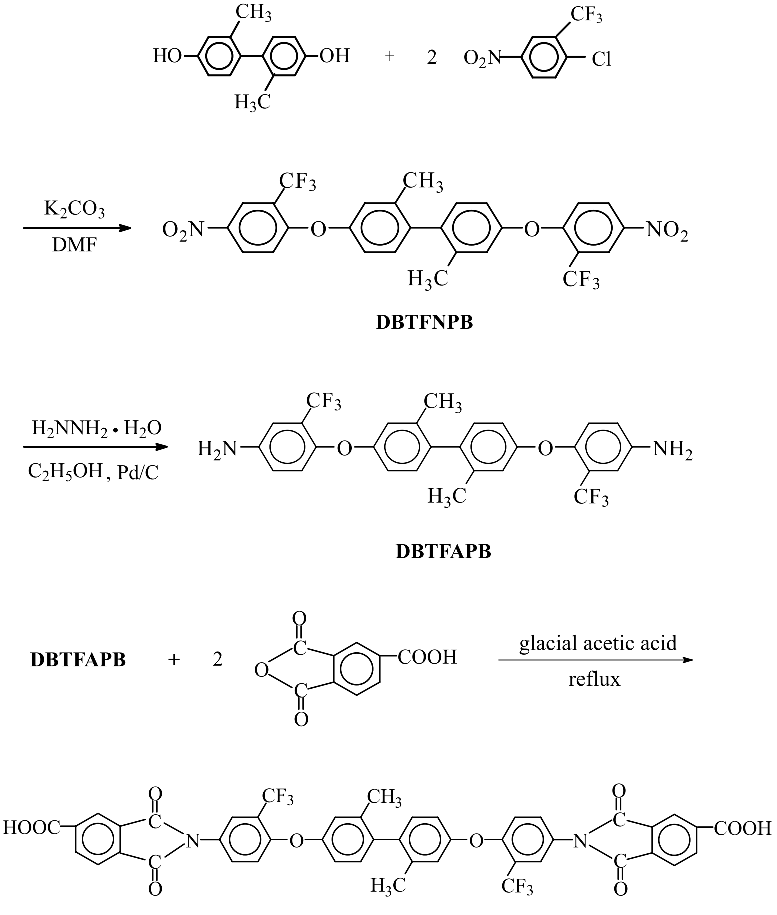
A mixture of 2,2′-dimethylbiphenyl-4,4′-diol [8,11,15] (8.00 g, 0.0373 mol), 2-chloro-5-nitrobenzotrifluoride (17.54 g, 0.0777 mol), potassium carbonate (11.13 g, 0.08 mol) and *N*,*N*-dimethylformamide (DMF, 65 ml) was refluxed for 8 h and the poured into methanol/water (1:1 by volume). The crude product was recrystallized from glacial acetic acid to provide brown needles (mp 236 °C by DSC) with 75% yield. The IR spectrum taken with KBr pellets exhibited absorptions at 1588 and 1335 cm^{-1} (NO_2), 1270 cm^{-1} (C–O–C) and 1108–1139 cm^{-1} (C–F). ^1H NMR ($CDCl_3$): δ(ppm) = 2.14 (s, 6H, H_a), 7.03–7.05 (d, 2H, H_b), 7.08, 7.10 (d, 4H, H_g, H_e), 7.23–7.27 (d, 2H, H_c), 8.34–8.37 (d, 2H, H_d) and 8.60 (s, 2H, H_f). ^{13}C NMR ($CDCl_3$): δ(ppm) = 20.27 (C_1), 117.48 (C_7), 118.13 (C_5), 119.23 (C_8), 120.62 (C_9), 120.88 (C_9), 121.40 (C_8, C_9), 121.14 (C_9), 123.58 (C_8), 122.23 (C_{11}), 125.75 (C_8), 124.04–124.16 (C_{14}), 129.10 (C_{12}), 131.63 (C_4), 138.61 (C_3), 139.31 (C_2), 142.01 (C_{13}), 153.61 (C_{10}) and 161.34 (C_6). Anal. Calcd for $C_{28}H_{18}O_6F_6N_2$: C, 56.77%; H, 3.06%; N, 4.74%; found: C, 56.82%; H, 3.09%; N, 4.55%. The reaction scheme is shown in Scheme 1.

2.3. Synthesis of 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-aminophenoxy)biphenyl (DBTFAPB)

The dinitro compound DBTFNPB (5.5 g, 0.01 mol), 0.06 g of 10% Pd/C, and 20 ml ethanol were taken in a three-necked flask and hydrazine monohydrate (10 ml) was added dropwise over a period of 30 min at 80 °C. Upon completing the addition, the reaction was continued at reflux temperature for another 24 h. The mixture was then filtered to remove Pd/C. After cooling, the precipitated crystals were isolated by filtration, recrystallized from ethanol, and dried in vacuum. The yield was 85% and the melting point was 47 °C (by DSC). The IR spectrum (KBr) exhibited absorptions at 3445, 3352 and 1606 cm^{-1} (N–H), 1228 cm^{-1} (C–O–C) and 1101–1141 cm^{-1} (C–F). ^1H NMR ($CDCl_3$): δ(ppm) = 2.03 (s, 6H, H_h), 3.76 (s, 4H, H_g), 6.78–6.80 (dd, 2H, H_b), 6.80–6.82 (dd, 2H, H_e), 6.89 (d, 2H, H_c), 6.93–6.95 (d, 2H, H_d), 6.99 (d, 2H, H_f) and 7.02–7.04 (d, 2H, H_a). ^{13}C NMR ($CDCl_3$): δ(ppm) = 20.28 (C_1), 113.11–113.22 (quartet, $^3J_{C-F}$ = 5.00 Hz, C_{14}), 114.93 (C_5), 119.15 (C_7), 119.65 (C_{12}), 120.33–126.84 (quartet, $^1J_{C-F}$ = 272.90 Hz, C_8), 122.50–123.46 (quartet, $^2J_{C-F}$ = 31.44 Hz, C_9), 122.78 (C_{11}), 130.96 (C_4), 135.95 (C_3), 138.19 (C_2), 142.66 (C_{13}), 146.54 (C_{10}) and 157.16 (C_6). Anal. Calcd for $C_{28}H_{22}O_2F_6N_2$: C, 63.16%; H, 4.16%; N, 5.26%; found: C, 62.83%; H, 4.23%; N, 5.21%. The reaction scheme is shown in Scheme 1. The single colorless crystals of diamine compound DBTFAPB grew during the slow crystallization of their ethanol solutions. A crystal size of $0.30 \times 0.20 \times 0.15$ mm^3 was used for X-ray structure determination. Crystal data for the compound DBTFAPB: crystallized in a triclinic system with space group $P1$ [weight-average molecular weight = 532.48, a = 8.1780(10) Å, b = 9.2760(10) Å, c = 17.0160(2) Å; α = 78.6450(10)°, β = 80.2260(10)°, γ = 85.5450(10)°, where D_c = 1.419 g/cm^3 for Z = 2 and V = 1245.87(3) Å^3]. Least-squares refinement based on 4349 independent reflections converged to the final R indices of R_1 = 0.0543 and wR_2 = 0.1579. Bond distance (Å) and bond angles (deg) for DBTFAPB were shown in Fig. 1.



DBTFAPB



Scheme 1. Synthesis of 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-aminophenoxy)biphenyl (DBTFAPB) and 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-trimellitimidophenoxy)biphenyl (DBTFTPB).

2.4. Synthesis of 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-trimellitimidophenoxy)biphenyl (DBTFTPB)

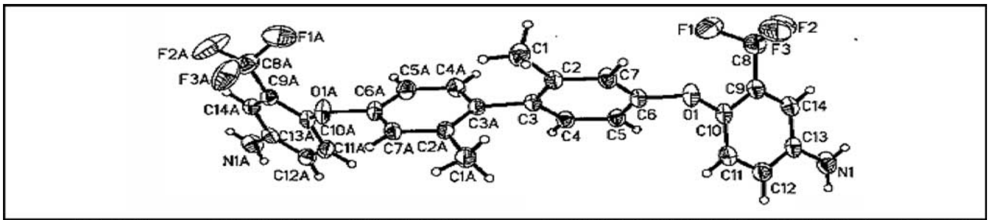
A flask was charged with a mixture of 1.5 g (0.0028 mol) of DBTFAPB, 1.4 g (7 mmol) of trimellitic anhydride and 20 ml of glacial acetic acid. The heterogeneous mixture was refluxed for 12 h. The reaction mixture was filtered to yield a yellow solid, which was rinsed with methanol to remove glacial acetic acid. The obtained crude product was washed several times with methanol, and purified by recrystallization from DMF/water (v/v = 4:1). The IR spectrum (KBr) exhibited absorptions at 2500–3700 cm^{-1} (C(O)O–H), 1773, 1715, and 1385 cm^{-1} and 1098–1128 cm^{-1} (C–F), confirming the presence of the imide ring and carboxylic acid groups in the structure. Yield = 75%, mp 329 °C (by DSC). ^1H NMR (DMSO-d_6): δ(ppm) = 2.01 (s, 6H); 7.01–7.04 (d, 2H); 7.16 (s, 2H); 7.19–7.21 (d, 2H); 7.26–7.28 (d, 2H); 7.76–7.78 (d, 2H); 7.96 (s, 2H); 8.05–8.08 (d, 2H); 8.29 (s, 2H); 8.39–8.41 (d, 2H). ^{13}C NMR (DMSO-d_6): δ(ppm) = 19.63, 116.66, 119.52, 119.59, 120.70, 121.99, 123.50, 123.88, 124.16, 126.25, 126.60, 131.15, 131.99, 133.34, 134.82, 135.59, 136.67, 136.87, 138.32, 154.52, 154.56, 165.80, 166.15. Anal. Calcd for $C_{46}H_{26}O_{10}F_6N_2$: C, 62.73%; H, 2.98%; N, 3.18%; found: C, 62.27%; H, 2.79%; N, 3.28%. The reaction scheme is shown in Scheme 1.

2.5. Polymerization

2.5.1. Polyamide PA-1

A flask was charged with a mixture of diamine DBTFAPB 0.5325 g (1 mmol), diacid I-1 0.1661 g (1 mmol), *N*-methyl-2-pyrrolidinone (NMP, 3 ml), pyridine (0.7 ml) triphenyl phosphite (TPP, 0.7 ml), and calcium chloride (0.3 g). It was carried out at 100 °C under argon atmosphere for 3 h. After cooling, the reaction mixture was poured into excess of methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried to afford PA-1. It was then washed with hot acetone using a Soxhlet extractor. The other polyamides (PA-2–PA-7) were prepared using similar procedures.

2.5.2. Polyimide PI-1. To the stirred solution of 0.5325 g (1 mmol) of DBTFAPB in 5 ml of DMAc, 0.4442 g (1 mmol)



F(1)-C(8)	1.333(3)	C(2A)-C(3A)	1.403(3)	C(10A)-C(11A)-C(12A)	120.4(2)
F(3)-C(8)	1.344(3)	C(4A)-C(5A)	1.383(3)	C(14A)-C(13A)-C(12A)	118.4(2)
O(1)-C(10)	1.395(3)	C(6A)-C(7A)	1.376(3)	C(12A)-C(13A)-N(1A)	120.8(2)
C(1)-C(2)	1.511(3)	C(9A)-C(10A)	1.383(3)	C(7)-C(2)-C(3)	119.2(2)
C(2)-C(3)	1.404(3)	C(10A)-C(11A)	1.379(3)	C(3)-C(2)-C(1)	122.0(2)
C(3)-C(3A)	1.493(3)	C(12A)-C(13A)	1.391(3)	C(4)-C(3)-C(3A)	120.2(2)
C(5)-C(6)	1.382(3)	C(6)-O(1)-C(10)	119.9(2)	C(5)-C(4)-C(3)	122.8(2)
C(8)-C(9)	1.484(4)	C(7)-C(2)-C(1)	118.8(2)	C(5)-C(6)-C(7)	120.0(2)
C(9)-C(10)	1.384(3)	C(4)-C(3)-C(2)	117.9(2)	C(7)-C(6)-O(1)	114.8(2)
C(11)-C(12)	1.378(3)	C(2)-C(3)-C(3A)	121.8(2)	F(1)-C(8)-F(2)	105.3(3)
C(13)-C(14)	1.379(4)	C(6)-C(5)-C(4)	118.2(2)	F(2)-C(8)-F(3)	106.0(2)
F(2A)-C(8A)	1.307(3)	C(5)-C(6)-O(1)	125.2(2)	F(2)-C(8)-C(9)	112.9(2)
O(1A)-C(10A)	1.383(3)	C(6)-C(7)-C(2)	121.7(2)	C(14)-C(9)-C(10)	119.6(2)
N(1A)-C(13A)	1.398(3)	F(1)-C(8)-F(3)	106.1(2)	C(10)-C(9)-C(8)	120.1(2)
C(2A)-C(7A)	1.397(3)	F(1)-C(8)-C(9)	114.1(2)	C(11)-C(10)-O(1)	121.5(2)
C(3A)-C(4A)	1.390(3)	F(3)-C(8)-C(9)	111.9(2)	C(12)-C(11)-C(10)	120.4(2)
C(5A)-C(6A)	1.374(3)	C(14)-C(9)-C(8)	120.1(2)	C(14)-C(13)-N(1)	120.6(2)
C(8A)-C(9A)	1.488(4)	C(11)-C(10)-C(9)	119.6(2)	N(1)-C(13)-C(12)	121.4(3)
C(9A)-C(14A)	1.395(3)	C(9)-C(10)-O(1)	118.6(2)	C(10A)-O(1A)-C(5A)	118.4(2)
C(11A)-C(12A)	1.382(3)	C(11)-C(12)-C(13)	120.9(2)	C(7A)-C(2A)-C(1A)	118.5(2)
C(13A)-C(14A)	1.377(3)	C(14)-C(13)-C(12)	118.0(2)	C(4A)-C(3A)-C(2A)	118.8(2)
F(2)-C(8)	1.338(3)	C(13)-C(14)-C(9)	121.5(2)	C(2A)-C(3A)-C(3)	121.5(2)
O(1)-C(6)	1.380(2)	C(7A)-C(2A)-C(3A)	118.6(2)	C(6A)-C(5A)-C(4A)	118.4(2)
N(1)-C(13)	1.389(3)	C(3A)-C(2A)-C(1A)	122.9(2)	C(5A)-C(6A)-O(1A)	122.5(2)
C(2)-C(7)	1.382(3)	C(4A)-C(3A)-C(3)	119.8(2)	C(6A)-C(7A)-C(2A)	121.0(2)
C(3)-C(4)	1.391(3)	C(5A)-C(4A)-C(3A)	122.2(2)	F(1A)-C(8A)-F(3A)	103.6(3)
C(4)-C(5)	1.387(3)	C(5A)-C(6A)-C(7A)	121.0(2)	F(1A)-C(8A)-C(9A)	113.0(3)
C(6)-C(7)	1.383(3)	C(7A)-C(6A)-O(1A)	116.4(2)	F(3A)-C(8A)-C(9A)	112.2(3)
C(9)-C(14)	1.387(3)	F(1A)-C(8A)-F(2A)	108.9(3)	C(10A)-C(9A)-C(8A)	120.5(2)
C(10)-C(11)	1.379(4)	F(2A)-C(8A)-F(3A)	104.4(3)	C(11A)-C(10A)-O(1A)	122.1(2)
C(12)-C(13)	1.394(4)	F(2A)-C(8A)-C(9A)	113.9(2)	O(1A)-C(10A)-C(9A)	118.2(2)
F(1A)-C(8A)	1.304(4)	C(10A)-C(9A)-C(14A)	119.8(2)	C(11A)-C(12A)-C(13A)	120.9(2)
F(3A)-C(8A)	1.347(4)	C(14A)-C(9A)-C(8A)	119.7(2)	C(14A)-C(13A)-N(1A)	120.8(2)
O(1A)-C(6A)	1.392(2)	C(11A)-C(10A)-C(9A)	119.5(2)	C(13A)-C(14A)-C(9A)	121.0(2)
C(1A)-C(2A)	1.504(3)				

Fig. 1. Structure refinement, bond distance (Å) and bond angles (deg) for DBTFAPB.

of dianhydride II-1 was gradually added. The mixture was stirred at room temperature for 2–4 h under argon atmosphere to form poly(amic acid). Chemical cyclodehydration was carried out by adding DMAc, and an equimolar mixture of acetic anhydride and pyridine into the above-mentioned poly(amic acid) solution with stirring at room temperature for 1 h, and then treated at 100 °C for 3 h. The polymer solution was poured into methanol. The precipitate was collected by filtration, washed thoroughly with methanol and hot water, and then dried at 100 °C under vacuum. The other polyimides (PI-2–PI-4) were prepared using similar procedures.

Poly(amide–imide) PAI-2. A mixture of diamine III-2 0.5325 g (1 mmol), DBTFTPB 0.8807 g (1 mmol), *N*-methyl-2-pyrrolidinone (NMP, 5 ml), pyridine (0.8 ml), triphenyl phosphite (TPP, 0.8 ml), and calcium chloride (0.4 g) was carried out at 100 °C under argon atmosphere for 3 h. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, which produced stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100 °C under vacuum. The other poly(amide–imide)s (PAI-1, PAI-3–PAI-5) were prepared using similar procedures.

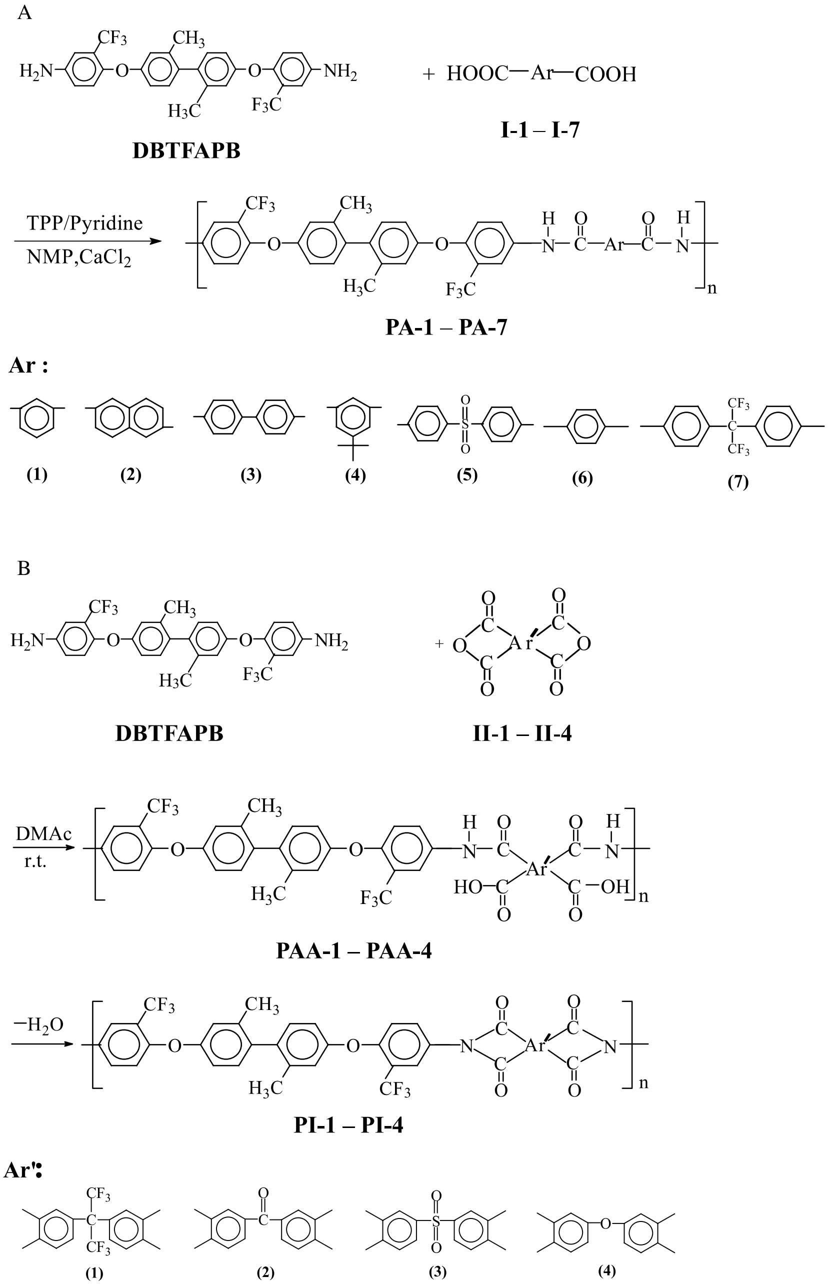
3. Measurements

Infrared (IR) spectra were recorded in the 4000–500 cm^{-1} range for the synthesized monomers and polymers on KBr disks (Bio-Rad FTS-3500 spectrometer). Single-crystal X-ray diffraction data were determined by Nonious CAD4 Kappa Axis XRD. The inherent viscosities of polymers were measured using an Ubbelohde viscometer. The NMR spectra were recorded using a BRUKER AVANCE 500 NMR (^{1}H at 500 MHz and ^{13}C at 125 MHz). Fraction of absorbed water (%) in polyimide films ($3.0\times1.0\times0.05\ \mathrm{cm}^3$) was determined by immersing in boiling deionized water (100 °C) in a 250 ml round-bottom flask fitted with a condenser for 24 h. This was then dried immediately and weighed to determine the water-uptake. Thermogravimetric data were obtained on a Du Pont 2200 apparatus in flowing nitrogen ($60\ \mathrm{cm}^3\ \mathrm{min}^{-1}$) at a heating rate of 20 °C min^{-1}. Differential scanning calorimetric analysis was performed on a differential scanning calorimeter (Du Pont 2000) at a heating rate of 10 °C min^{-1}. Tensile properties were determined from stress–strain curves obtained with an Orientec Tensilon with a load cell of 10 kg. A gauge of 3 cm and a strain rate of 2 cm min^{-1} were used for this study. Measurements were performed at room temperature on 0.5 cm wide, 6 cm long, and 0.5 mm thick film specimens. The in-plane linear coefficient of thermal expansion (CTE) was obtained from a thermomechanical analyzer TMA-2940 (10 °C min^{-1} from 30 to 300 °C, 0.05 N). The CTE value was measured on the temperature scale between 50 and 150 °C. Dielectric constants were measured using a dielectric analyzer (TA Instruments DEA 2970) at a frequency of 1 KHz. UV–vis spectra of the polymer films were recorded on a Jasco V-550 spectrophotometer.

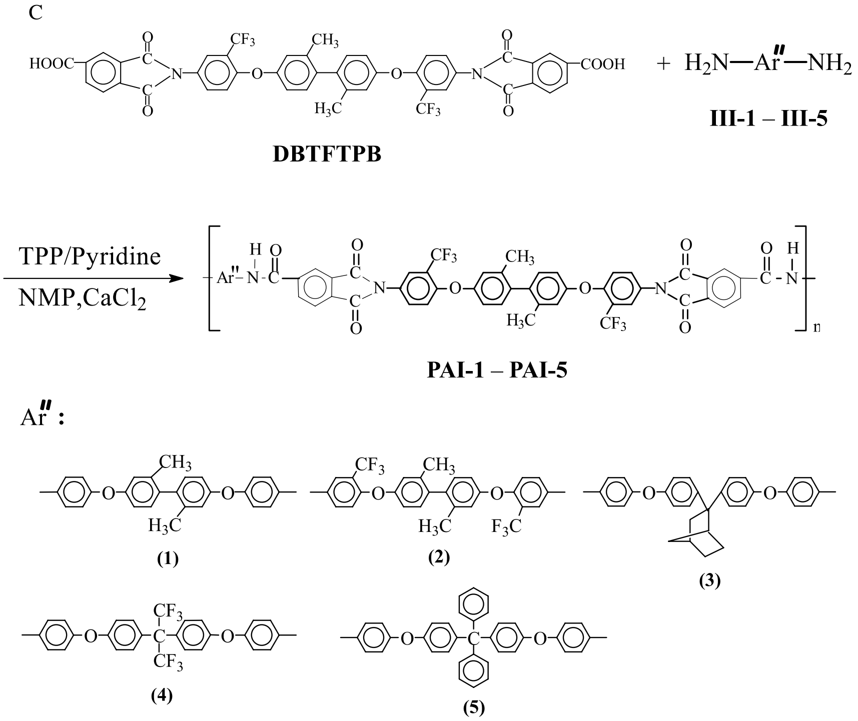
Refractive index was measured by a Metricon model PC-2010 prism coupler at room temperature in open air. The measurements were made at a wavelength of 632.8 nm (He–Ne laser). Using parallel (TE) and perpendicularly (TM) polarized laser light, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the sample films were determined. Weight-average (M_{w}) and number-average (M_{n}) molecular weights were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns $300\times7.8\ \mathrm{mm}^2$ (guard, 10^5, 10^4, 10^3, 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1.0 ml min^{-1}) as the eluent. The eluents were monitored with a RI detector (Schambeck SFD GMBH RI 2000) and UV detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard.

4. Results and discussion

4.1. Synthesis of monomer. Scheme 1 shows the synthetic route to diamine 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-



Scheme 2. Preparation of various polyamides, polyimides and poly(amide–imide)s.



Scheme 2 (*continued*)

aminophenoxy)biphenyl (DBTFAPB) and diimide diacid 2,2′-dimethyl-4,4′-bis(2-trifluoromethyl-4-trimellitimidophenoxy)-biphenyl (DBTFTPB).

The dinitro compound (DBTFNPB) was reduced in ethanol in the presence of hydrazine and a catalytic amount of palladium on activated carbon at 80 °C to produce diamine (DBTFAPB). The structures of these compounds were confirmed by elemental analysis, IR, X-ray crystallographic analysis, and NMR spectroscopy. As indicated in Section 2, the elemental analysis data of the dinitro and diamine compounds were found to correspond well with the calculated values for their structures. Absorptions appearing around 1335 and 1588 cm^{-1} are due to symmetric and asymmetric stretching of $-NO_2$ group in the IR spectra of the dinitro DBTFNPB. The characteristic absorption of nitro groups disappeared and the characteristic bonds of amino groups at 3445 and 3352 cm^{-1} (N–H stretching) and 1606 cm^{-1} (N–H bending) appeared after reduction.

In the ^{1}H NMR spectrum of DBTFAPB, the signals of aromatic protons appear in the range of 6.78–7.04 ppm, and the characteristic resonance signal at 3.76 ppm is due to the amino group. As shown in the experimental part, the ^{13}C NMR spectra of both DBTFNPB and DBTFAPB exhibited similar coupling patterns. There are three quartets in the region of 110–130 ppm due to the heteronuclear ^{13}C–^{19}F coupling. The coupling constant of one-bond C–F is about 273 Hz, two-bond is about 31 Hz, and three-bond is 5 Hz, respectively. Those results clearly confirm that the structure of diamine DBTFAPB prepared herein is consistent with that of the proposed structure.

The diimide–dicarboxylic acid (DBTFTPB) was obtained by reacting diamine DBTFAPB with 2 mol equiv. of trimellitic anhydride (TMA) in refluxing glacial acetic acid to form an amic acid intermediate in homogeneous, and then was imidized to be precipitated from the reaction mixture. Elemental analysis, IR, and NMR spectroscopies confirmed the structure of this compound. The elemental analysis data of diimide–dicarboxylic acid compound was found to agree well with the calculated values of their structures. The IR spectrum showed the characteristic absorption bands around 2500–3700 cm^{-1} (–OH, carboxylic acid), 1773 cm^{-1} (imide C=O asymmetrical stretching), and 1715 cm^{-1} (imide C=O symmetrical stretching and acid C=O stretching), confirming the presence of imide ring and carboxylic acid groups in the structure. The ^{1}H NMR spectrum of DBTFTPB showed three proton signals around the downfield regions (8.05–8.41 ppm) due to the trimellitic acid moiety. The ^{13}C spectrum was observed with the carbonyl carbons of carboxylic acid and imide groups resonating in the downfield at 165.8 and 166.2 ppm, respectively. It also exhibited similar heteronuclear ^{13}C–^{19}F coupling pattern in the region of 110–130 ppm. The results of the NMR spectra provided clear evidence to the proposed structure of the diimide–dicarboxylic acid monomer.

4.2. Synthesis of polymer. The preparation of these polyamides (PAs) (PA-1–PA-7), polyimides (PIs) (PI-1–PI-4) and poly (amide–imide)s (PAIs) (PAI-1–PAI-5) are shown in Scheme 2.

Both PAs and PAIs were prepared by Yamazaki–Higashi phosphorylation polyamidation technique [20]. PAs can be obtained from the reaction of the diamine DBTFAPB and various aromatic dicarboxylic acids and PAIs can be obtained from the reaction of the diimide–dicarboxylic acid DBTFTPB and various aromatic diamines. All the PAs and PAIs remained soluble in the reaction medium, thus permitting an increase in their molecular weight and giving viscous solutions. PAs and PAIs had inherent viscosities in the range of 0.66–1.34 dL g^{-1} (Table 1). Number-average (M_n) and weight-average (M_w) molecular weights of the polymers were found to be in the range of 2.1×10^4–7.3×10^4 and 4.5×10^4–17.9×10^4, respectively (Table 1).

The molecular weight of the polymers was high enough to obtain flexible and tough polymer films by casting from their DMAc solutions. The compositions of these polyamides and poly(amide–imide)s were confirmed by their elemental analyses (Table 1). They were almost in good agreement with the calculated values for the proposed structures. For PAs and PAIs, the values of carbon were lower than the calculated values for the proposed structures. This finding may be attributed to the hygroscopic characteristics of the amide group [21]. The amount of absorbed water of these PAs and

Table 1
Inherent viscosity, molecular weight and elemental analysis of various polymers

Polymer code	η_{inh} (dL g^{-1})[a]	$\bar{M}_n \times 10^{-4}$[b]	$\bar{M}_w \times 10^{-4}$[b]	Elemental analysis (%)				Fraction of absorbed water (%)
					C	H	N	
PA-1	1.26	[c]	[c]	Calcd	65.26	3.65	4.23	2.20[d]
				Found	64.18	3.82	3.98	
				Corrtd[e]	65.62	3.74	4.07	
PA-2	1.34	6.3	11.5	Calcd	67.42	3.68	3.93	3.17[d]
				Found	65.82	3.90	4.10	
				Corrtd[e]	67.97	3.78	4.23	
PA-3	1.14	[c]	[c]	Calcd	68.29	3.82	3.79	2.00[d]
				Found	65.55	4.03	3.56	
				Corrtd[e]	66.88	3.95	3.63	
PA-4	1.10	4.3	10.5	Calcd	66.85	4.49	3.90	2.43[d]
				Found	65.71	4.63	3.66	
				Corrtd[e]	67.34	4.52	3.75	
PA-5	0.93	2.4	5.0	Calcd	62.84	3.52	3.49	2.20[d]
				Found	61.36	3.79	3.32	
				Corrtd[e]	62.77	3.71	3.39	
PA-6	0.77	[c]	[c]	Calcd	65.26	3.65	4.23	3.20[d]
				Found	63.31	3.79	4.20	
				Corrtd[e]	65.40	3.67	4.33	
PA-7	0.66	4.2	7.7	Calcd	60.82	3.18	3.15	1.79[d]
				Found	59.84	3.39	3.08	
				Corrtd[e]	60.93	3.33	3.14	
PI-1	0.75	6.1	17.9	Calcd	60.01	2.57	2.98	0.29[f,g]
				Found	59.00	2.21	3.11	
PI-2	0.85	[c]	[c]	Calcd	66.02	2.95	3.42	0.43[f,g]
				Found	65.01	3.35	3.62	
PI-3	0.69	3.4	10.7	Calcd	61.83	2.83	3.28	0.60[f,g]
				Found	61.80	2.46	3.53	
PI-4	0.60	2.1	4.5	Calcd	65.51	3.00	3.47	0.46[f,g]
				Found	64.76	3.38	3.78	
PAI-1	1.00	[c]	[c]	Calcd	69.68	3.74	4.51	2.52[e]
				Found	67.89	3.91	4.36	
				Corrtd[d]	69.64	3.81	4.47	
PAI-2	0.89	7.3	16.2	Calcd	64.54	3.22	4.07	2.04[e]
				Found	62.64	3.47	3.92	
				Corrtd[d]	63.94	3.40	4.00	
PAI-3	1.12	[c]	[c]	Calcd	70.75	4.00	4.29	2.84[e]
				Found	68.73	4.27	4.10	
				Corrtd[d]	70.74	4.15	4.22	
PAI-4	0.68	3.0	6.3	Calcd	64.32	3.11	4.11	1.90[e]
				Found	62.87	3.35	3.74	
				Corrtd[d]	64.09	3.29	3.82	
PAI-5	1.17	[c]	[c]	Calcd	72.27	3.80	4.06	2.49[e]
				Found	70.86	3.63	3.58	
				Corrtd[d]	72.67	3.54	3.67	

[a] Measured in DMAc at a concentration of 0.5 g dL^{-1} at 30 °C.

[b] Measured by GPC in THF; polystyrene was used as standard.

[c] Polymer could not soluble in THF at room temperature.

[d] Corrected value = found value/(1 + fraction of absorbed water) where + for H, − for C and N.

[e] Fraction of absorbed water (%) = (sample mass at room temperature − sample mass after drying under vacuum at 100 °C)/sample mass at room temperature.

[f] Fraction of absorbed water (%) = $(W_2-W_1)/W_1$, where W_2 is the weight of the film samples after immersion in water, and W_1 is the initial weight of the samples.

[g] Reference: Liu JG, Li ZX, Wu TJ, Zhou HW, Wang SY, Yang SY. J Polym Sci, Part A: Polym Chem 2002; 40: 1583.

PAIs were in the ranges of 1.79–3.20% and 1.90–2.84%, respectively. Fluorine substitution almost universally results in lower water absorption. PA-7, PAI-2 and PAI-4 had the lowest values for water absorption. The hydrophobic nature imparted by the trifluoromethyl group render PA-7, PAI-2 and PAI-4 less water absorbing as compared to other polymers [21,22]. The IR spectra of PAs and PAIs showed characteristic absorptions of the amide groups around 3300 cm^{-1} which were peculiar to N–H stretching, and the 1660 cm^{-1} band was due to carbonyl stretching. The PAIs also showed characteristic absorption bands for the imide ring around 1780 and 1722 cm^{-1} that were peculiar to the asymmetrical and symmetrical carbonyl stretching vibrations, respectively.

Polyimides (PIs) were prepared by the conventional two-step polymerization method, as shown in Scheme 2, involving ring-opening polyaddition forming poly(amic acid) (PAA) and subsequent thermal or chemical imidization. Chemical imidization of PAAs with a dehydrating agent such as a mixture of acetic anhydride and pyridine was also effective in obtaining PIs. Before adding the dehydrating agent, extra-dry DMAc must be added in the PAAs solution to prevent gelation while imidization. The inherent viscosities of all PIs are summarized in Table 1. By the chemical procedure, the resulting PIs were found to have inherent viscosities of 0.60–0.85 dL g^{-1} in concentrated DMAc. The molecular weights of PIs were sufficient to permit the casting of tough and flexible films. The elemental analysis values of these PIs were in good agreement with their respective structures (Table 1). PIs exhibited low water-uptake values in the range of 0.29–0.60%. The PI-1 showed the lowest value, which might be attributed to the presence of hydrophobic trifluoromethyl and hexafluoroisopropylidene substitution in the polymer backbones. The structure of polymers could be further identified by IR spectroscopy. The characteristic bands around 1720 and 1780 cm^{-1} are attributed to the symmetric and asymmetric stretches of imide carbonyl groups, respectively. The C–N stretching absorption at 1375 cm^{-1} confirmed the imide formation.

4.3. Properties of polymers. Table 2 summarizes the solubility and film characteristics of these polymers.

All the polymers exhibited excellent solubility in a variety of solvents such as *N*-methyl-2-pyrrolidinone (NMP),

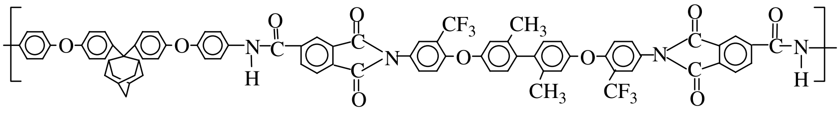
Table 2
Solubilities and film properties of various polymers

Polymer code	Solubility of polymers[a]								Film characteristics
	NMP	DMAc	DMF	DMSO	Pyridine	THF	γ-Butyrolactone	Cyclohexanone	
PA-1	++	++	++	++	++	+−	+	++	Very light yellow to colorless, transparent, flexible
PA-2	++	++	++	++	++	++	+	++	Very light yellow to colorless, transparent, flexible
PA-3	++	++	++	++	++	+	+	+−	Very light yellow to colorless, transparent, flexible
PA-4	++	++	++	++	++	++	++	++	Very light yellow to colorless, transparent, flexible
PA-5	++	++	++	++	++	++	++	++	Very light yellow to colorless, transparent, flexible
PA-6	++	++	++	++	++	+	++	++	Very light yellow to colorless, transparent, flexible
PA-7	++	++	++	++	++	++	++	++	Very light yellow to colorless, transparent, flexible
PI-1	++	++	++	++	++	++	++	++	Very light yellow to colorless, transparent, flexible
PI-2	++	++	++	+−	++	+	+	+	Very light yellow to colorless, transparent, flexible
PI-3	++	++	++	+−	++	++	++	++	Very light brown to colorless, transparent, flexible
PI-4	++	++	++	+	++	++	++	++	Very light yellow to colorless, transparent, flexible
PAI-1	++	++	++	+	++	+−	+−	+	Very light brown to colorless, transparent, flexible
PAI-2	++	++	++	++	++	++	++	++	Very light yellow to colorless, transparent, flexible
PAI-3	++	++	++	++	+	+	+−	++	Very light brown to colorless, transparent, flexible
PAI-4	++	++	++	++	++	++	+	++	Very light brown to colorless, transparent, flexible
PAI-5	++	++	++	++	++	+	+	++	Very light brown to colorless, transparent, flexible

Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran.

[a] Solubility: ++, soluble at room temperature; +, soluble on heating at 70 °C; +−, partially soluble on heating at 70 °C; −, insoluble on heating at 70 °C.

N,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine, THF, γ-butyrolactone and cyclohexanone at room temperature or upon heating at 70 °C. This result demonstrated that the polymers containing fluorine and with noncoplanar conformation improved their solubility in the organic solvents. Among these polymers, PA-4, PA-5, PA-7, PI-1 and PI-3 containing *tert*-butyl, flexible sulfonyl, hexafluoroisopropylidene, noncoplanar biphenylene and trifluoromethyl substitution, showed better solubility than the others and were easily soluble at room temperature. PAI-2 combines noncoplanar biphenylene and trifluoromethyl substitution and showed better solubility and was also easily soluble at room temperature. The fluorine-containing lead to rigid polymer backbone, which can improve the solubility of the polymers [23]. The fluorine-containing polymers were very light yellow or nearly colorless. Many non-fluorinated polymer films are known to be yellow to dark amber in color, whereas the fluorinated polymer films are almost colorless.



Ad-PAI

Thermal properties of the polyamides, polyimides and poly(amide–imide)s are tabulated in Table 3. Glass transition temperatures (T_g) of the polyamides, determined by differential scanning calorimetry (DSC), were found to be in the range of 230–255 °C. The increasing order of T_g generally corresponds to the stiffness and bulkiness of the dicarboxylic acid moiety [6,24]. The T_g of PA-4 is higher than PA-1 due to the presence of bulky *t*-butyl group in the polymer chain. The T_g of PIs and PAIs were evaluated by dynamic mechanical analysis (DMA) because there was no distinct T_g that could be observed from the heating trace in the DSC. Therefore, the T_g values of the PIs and PAIs were determined by DMA using film species. They were found in the range of 235–265 °C. The glass transition temperature (T_g) of the polyimides was affected by dianhydride moieties, which shows the following order: II-3(DSDA) > II-1(6FDA) > II-2(BTDA) > II-4(OPDA) as shown in Table 3 [25,26]. Remarkably, the Ad-PAI polymer containing adamantane cardo group was found to have higher T_g value (T_g = 284 °C) than the other PAIs (T_g = 240–256 °C) although it has relatively lower solubility than the others, such as in DMSO, γ-butyrolactone and cyclohexanone. In general, polymer with cardo groups showed high T_g value due to the bulky pendent group, which inhibited the free rotation of the polymer backbone [27].

Table 3
Thermal properties of various polymers

Polymer code	T_g (°C)[a]	$T_{d,10}$ (°C)[b]		Char yield (%)[c]	CTE (ppm/°C)[d]
		In N_2	In air		
PA-1	230[a]	482	461	55	66
PA-2	247[a]	487	463	56	51
PA-3	239[a]	467	457	50	55
PA-4	255[a]	486	442	52	136
PA-5	233[a]	465	453	51	89
PA-6	230[a]	476	439	47	61
PA-7	234[a]	488	456	53	105
PI-1	261[e]	552	543	57	95
PI-2	239[e]	503	502	59	62
PI-3	265[e]	462	464	56	79
PI-4	235[e]	525	507	58	82
PAI-1	250[e]	500	459	53	62
PAI-2	255[e]	505	502	58	68
PAI-3	261[e]	484	495	54	50
PAI-4	240[e]	516	498	56	64
PAI-5	256[e]	520	488	61	63

[a] From DSC measurements conducted at a heating rate of 10 °C min^{-1}.

[b] Temperature at 10% weight loss ($T_{d,10}$) was determined by TG at a heating rate of 20 °C min^{-1}.

[c] Char yield at 800 °C in nitrogen.

[d] The CTE value was measured on the temperature scale between 50 and 150 °C.

[e] From DMA measurements conducted at a heating rate of 5 °C min^{-1}.

The 10% weight loss temperature ($T_{d,10}$) as well as the anaerobic char yield at 800 °C in nitrogen, measured by TGA, are also summarized in Table 3. All the polymers exhibited excellent thermal stability. They started to decompose around or above 460 °C in nitrogen atmosphere and lost 10% weight between 462–552 and 439–543 °C in nitrogen and air atmosphere, respectively. The polymers had char yields above 47% at 800 °C in nitrogen. It implied that these polymers with trifluoromethyl and noncoplanar groups in the polymer backbone showed excellent thermal stability.

Table 4
Mechanical properties of various polymers

Polymer code	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
PA-1	102	10	2.2
PA-2	110	28	2.6
PA-3	98	15	2.0
PA-4	95	9	1.9
PA-5	92	12	2.0
PA-6	88	12	2.0
PA-7	98	7	1.9
PI-1	84	7	2.0
PI-2	89	6	2.3
PI-3	82	6	2.0
PI-4	82	7	1.9
PAI-1	112	9	2.5
PAI-2	104	11	2.2
PAI-3	124	9	2.9
PAI-4	98	6	2.1
PAI-5	108	7	2.3

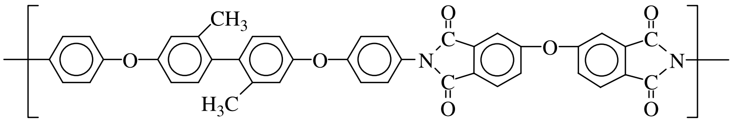
Table 5
Optical properties and dielectric constants of various polymer films

Polymer code	Cut-off wavelength (nm)	80% Transmission wavelength (nm)	n_{TE}	n_{TM}	n_{AV}[a]	Birefringence ($n_{TE}-n_{TM}$)	Thickness (μm)	Dielectric constant[b]
PA-1	350	488	1.5985	1.5867	1.5945	0.0118	66	3.52
PA-2	377	500	1.6230	1.5904	1.6121	0.0326	84	3.75
PA-3	369	556	1.6057	1.5644	1.5919	0.0413	65	3.53
PA-4	362	494	1.5824	1.5731	1.5793	0.0093	74	3.22
PA-5	388	528	1.5933	1.5676	1.5847	0.0257	75	3.07
PA-6	371	548	1.6022	1.5935	1.5993	0.0087	64	3.63
PA-7	347	470	1.5523	1.5446	1.5497	0.0077	62	2.87
PI-1	388	452	1.5637	1.5591	1.5622	0.0046	87	3.05
PI-2	384	484	1.6233	1.6142	1.6203	0.0091	76	3.32
PI-3	371	470	1.5903	1.5848	1.5885	0.0055	76	3.59
PI-4	383	474	1.6106	1.6002	1.6071	0.0104	86	3.85
PAI-1	389	477	1.6587	1.6489	1.6554	0.0098	76	4.03
PAI-2	381	447	1.6137	1.6063	1.6112	0.0074	74	3.27
PAI-3	388	473	1.5752	1.5702	1.5735	0.0050	74	3.99
PAI-4	402	476	1.6158	1.6047	1.6121	0.0111	72	3.69
PAI-5	414	486	1.6631	1.6327	1.6530	0.0304	72	3.90

[a] Average refractive index; $n_{AV}=(2n_{TE}+n_{TM})/3$.

[b] Dielectric constants were obtained in the frequency 1 kHz on thin films.

All the new polymers possessed outstanding film-forming properties. Transparent flexible films were obtained by solution casting from DMAc on glass substrates. The mechanical properties of the PA, PI and PAI films are shown in Table 4. The polymer films had a tensile strength in the range of 82–124 MPa, elongation at break ranged from 6 to 28%, and tensile modulus ranged from 1.9 to 2.9 GPa. Most of the polymer films exhibited high tensile strength; thus they could be considered as strong materials.



Ref-A

The optical properties of the polyamides, polyimides and poly(amide–imide)s could also be elucidated from the cut-off wavelength observed in the UV–visible spectra and the results are listed in Table 5. In those polymers, the cut-off wavelength ranged from 347 to 414 nm and the 80% transmission wavelength ranged from 447 to 556 nm.

The PA-7, PI-1 and PAI-2 exhibited the lowest wavelength of transmittance among the PAs, PIs and PAIs (Table 5). The polyimide film PI-1 derived from II-1(6FDA) also exhibited high transparency, and might be attributed to the bulky trifluoromethyl group in the dianhydride units, which separated chromaphoric groups and interrupted the intramolecular conjugation. Hasegawa and Horie [28] reported earlier about obtaining transparent PIs by using lower electron-accepting dianhydrides and lower electron-donating diamines as monomers for weakening both intra- and inter-molecular charge-transfer interactions. The optical properties of PA-7 and PAI-2 were the same as that of PI-1.

Comparing PI-4 with Ref-A without trifluoromethyl groups as shown in Fig. 2, PI-4 has lower cut-off wavelength and 80% transmission wavelength than in Ref-A. These results were attributed to the presence of trifluoromethyl substituents in the diamine. In addition, a secondary positive effect of the trifluoromethyl substituents on the film transparency is weakening of intermolecular cohesive force due to lower polarizability of the C–F linkage, and then reduces the formation of the interchain charge-transfer complex [26].

The refractive indices in both the in-plane and out-of-plane directions are shown in Table 5. These refractive indices are attributed to the polarizabilities of atoms consisting of polymer backbones and their chemical bonds. In general, higher polarizability causes a higher dipole moment under electromagnetic field, providing a higher refractive index. The fluorine atom exhibits a relatively low polarizability because of its high electronegativity [29]. Both oxygen and hydrogen

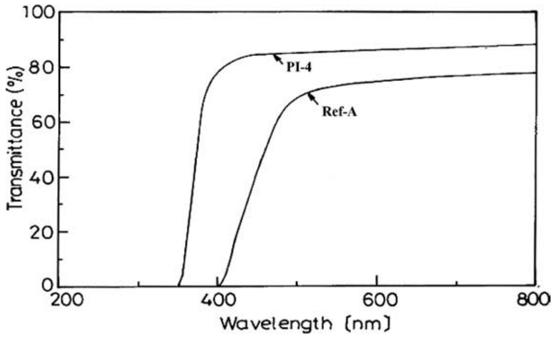
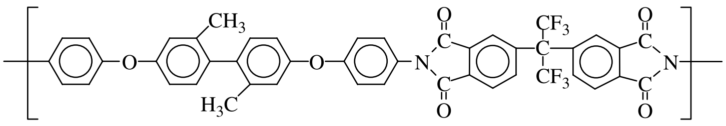


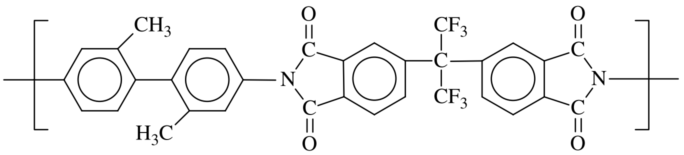
Fig. 2. Comparison of UV spectrum of PI-4 and Ref A.

have intermediate polarizabilities. When these atoms are involved in the formation of chemical bonds, the polarizabilities of the chemical bonds also contribute to the refractive index. Therefore, the incorporation of low polarizable atoms, as well as low polarizable chemical bonds into the polymer chain can reduce the refractive index. In addition, the reduction of refractive index due to the incorporation of side groups is also contributed in part from the increase in free volume of the polymer caused by the steric bulkiness of the side group. As the fractional free volume increases, the refractive index decreased. Polyimide PI-1 has the lowest refractive index (1.5622), which is contributed from the trifluoromethyl and hexfluorohexafluoropropane (6F) groups because of the low electronic polarizability as well as the dielectric constant. Incorporation of fluorine in the polymer backbone increases the free volume. It can be attributed to the greater steric volume of fluorine relative to hydrogen, which may interfere with efficient chain packing [30]. Similarly PA-7 has a lowest refractive index (1.5497) among polyamides. For poly(amide–imide)s PAI-3 has the lowest refractive index (1.5735) due to the pendent cardo group and increase in the free volume that effect chain packing in the polymer backbone. Similarly, Ad-PAI has low refractive index (1.5810) due to the pendent cardo group. For comparison, PAI-2 has four trifluoromethyl substitutions on the side chain leading to larger free volume and low refractive index (1.6112) than PAI-1 (1.6554). Birefringence expresses the level of optical anisotropy in the film, and it is defined as the difference in refractive index between two orthogonal planes of polarization. For polyamide films, the birefringence varied in the range of 0.0077–0.0413. Polyimide derived from 6FDA (PI-1) has lowest birefringence due to large fractional volume of trifluoromethyl and hexfluorohexafluoropropane (6F). Similarly, PAI-1 and PAI-2 showed low birefringence. Ad-PAI showed lower birefringence. Matsumoto [31] prepared semi- and non-aromatic PIs and showed that these PIs have very low birefringence. In this study, the introduction of aliphatic unit into a polymer backbone is expected to be effective for birefringence such as PAI-3 (0.0050). The electrical properties were measured using a dielectric analyzer (parallel-plate capacitor method) at a frequency of 1 kHz on thin films. The results of the electrical properties are listed in Table 5. PA, PI and PAI solutions were casting into films from DMAc and their film thickness were in the range of 62–87 μm. Dielectric constants of PIs measured at 1 kHz were in the range of 3.05–3.85; some of them are lower than that of commercially available polyimide film, Kapton H (3.50, 75 μm, 1 kHz) [32].

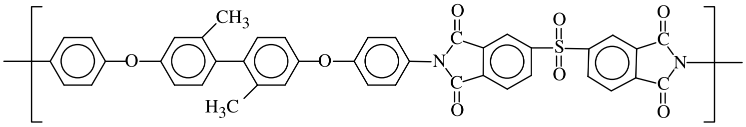
In particular, the dielectric constant of polyimide PI-1 containing trifluoromethyl and hexafluoropropane (6F) groups was quite low (3.05, 87 μm, 1 kHz). For comparison, Ref-B (3.78, 72 μm, 1 kHz), Ref-C (4.95, 61 μm, 1 kHz) and Ref-D (4.28, 83 μm, 1 kHz) were prepared and shown to have relatively higher dielectric constants. The low dielectric constant could be attributed to the presence of trifluoromethyl group, which resulted in efficient chain packing and increased free volume. The strong electronegativity of fluorine resulted in low polarizability of C–F bonds, thereby decreasing the dielectric constants. The dielectric constants of PA-7 and PAI-2 were the same as that of PI-1.



Ref-B



Ref-C



Ref-D

5. Conclusions

A series of highly organosoluble noncoplanar polyamides, polyimides and poly(amide–imide)s has been synthesized by polycondensation. The fluorine-containing polymers were almost soluble in all the organic solvents tested in this study at room temperature and were entirely transparent and colorless. The glass transition temperatures (T_gs) of all fluorine-containing polymers were in excess of 230 °C as measured by DSC or DMA. These polymer films showed excellent mechanical properties, as well as good thermo-oxidative stability, low dielectric constants, low refractive indices and low birefringence. Trifluoromethyl substitution was also shown to reduce moisture absorption. These characteristics indicate that fluoro-containing polymers are promising materials for optical communication applications.

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