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New Organosoluble Polyimides with Low Dielectric Constants Derived from Bis[4-(2-Trifluoromethyl-4-aminophenoxy)phenyl] Diphenylmethylene

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Summary: A new kink diamine with trifluoromethyl group on either side, bis[4-(2-trifluoromethyl-4-aminophenoxy)phenyl]diphenylmethane(**BTFAPDM**), was reacted with various aromatic dianhydrides to prepare polyimides via poly (amic acid) precursors followed by thermal or chemical imidization. Polyimides were prepared using 3,3', 4,4'-biphenyltetracarboxylic dianhydride(1), 4,4'-oxydiphthalic anhydride(2), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (3), 4,4'-sulfonyldiphthalic anhydride(4), and 4,4'-hexafluoroisopropylidene-diphathalic anhydride(5). The fluoro-polyimides exhibited low dielectric constants between 2.46 and 2.98, light color, and excellent high solubility. They exhibited glass transition temperatures between 227 and 253°C, and possessed a coefficient of thermal expansion (CTE) of 60-88 ppm/°C. Polymers **PI-2**, **PI-3**, **PI-4**, **PI-5** showed excellent solubility in the organic solvents: *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine and tetrahydrofuran (THF). Inherent viscosity of the polyimides were found to range between 0.58 and 0.72 dLg-1. Thermogravimetric analysis of the polyimides revealed a high thermal stability decomposition temperature in excess of 500°C in nitrogen. Temperature at 10 % weight loss was found to be in the range 506-563°C and 498-557°C in nitrogen and air, respectively. The polyimide films had a tensile strength in the range 75-87 MPa; tensile modulus, 1.5-2.2 GPa; and elongation at break, 6-7%.

Keywords: bis[4-(2-trifluoromethyl-4-aminophenoxy)phenyl]diphenylmethane-(BTFAPDM), dielectric constants, kink, polyimide, trifluoromethyl

Introduction

Aromatic polyimides are thermally stable polymers that exhibit excellent mechanical strength and stability. During the past decade, interests in these polymers have risen in response to increasing technological applications in a variety of fields such as aerospace,

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automobile, and microelectronics.[1] Generally, aromatic polyimides are insoluble in organic solvents, and have extremely high glass transition or melt-temperatures, which preclude melt processing. Hence, a great deal of efforts have been made to improve the processing characteristics of these intractable polymers. One of the successful approaches to improve solubility and processability of polyimides with minimal detrimental effect on their high thermal stability is the introduction of bulky substituents[2-4] or pendent groups[5,6] along the polymer backbone.

A successful approach that has improved the solubility and processability of polyimides is the introduction of kink linkages such as ether, sulfone, ketone, and methylene groups.[7-9] The most effective approach to obtain organo–soluble polyimides is the incorporation of substituted methylene linkages, such as isopropylidene[10-13] and hexafluoroisopropylidene[14,15] groups, which provides kinks in the backbone leading to an increased solubility of the polymer. Recently, we have reported polyimides with fluorine-containing kinks along the backbone [15]. It was observed that polyimides containing kink unit exhibit good solubility and mechanical property, and higher thermal stability.

In general, the solubility of polyimides can be improved by introducing flexible or bulky pendent groups such as phenyl,[16] cardo,[17] and fluorine–containing groups[18,19] on polymer backbone. Trifluoromethyl is an effective substituent that can improve the solubility[20] of polyimides without sacrificing the thermal, mechanical, and dielectric properties. Other special features of trifluoromethyl–containing polyimides are low dielectric constants and colorlessness. Hence, considerable attention has been devoted to the trifluoromethyl–containing polyimides in recent years. The reactivity of aromatic diamine, the monomer of polyimide, is greatly dependent on the chemical feature and position of the fluorine–containing substituents in the monomer because of the low polarizability and high electronegativity of fluorine atoms. Usually, aromatic diamines with fluorine or fluorinated moieties ortho to the amino groups yield low molecular weight polyimide by the conventional polycondensation procedure. Therefore, high reactive fluorine–containing aromatic diamines are required.

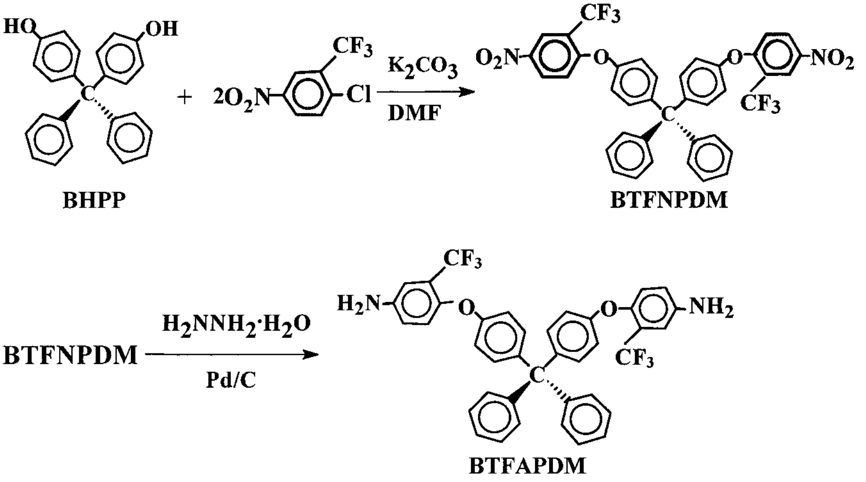
Experimental

Materials

Bis(4-hydroxyphenyl)diphenylmethane (**BHPP**) was successfully prepared by refluxing a mixture of dichlorodiphenylmethane and phenol (molar ratio 1:2) in xylene. Reagent grade aromatic dianhydrides such as 3,3',4,4'-biphenyltetracarboxylic dianhydride (**DA1**, from CHRISKEV), 4,4'-oxydiphthalic anhydride (**DA2**, from TCI), 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (**DA3**, from CHRISKEV), 4,4'-sulfonyldiphthalic anhydride (**DA4**, from New Japan Chemical Co.), and 4,4'-hexafluoroisopropylidenediphathalic anhydride (**DA5**, from CHRISKEV) were recrystallized from acetic anhydride prior to use. *N,N*-Dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF) and pyridine were vacuum distilled over calcium hydride prior to use.

Monomers Synthesis

Scheme 1 illustrates the synthesis route to diamine bis[4-(2-trifluoromethyl–4-aminophenoxy) phenyl] diphenylmethane (**BTFAPDM**).



Scheme 1. Synthesis route to diamine bis[4-(2-trifluoromethyl–4-aminophenoxy) phenyl] diphenylmethane (**BTFAPDM**).

Bis[4-(2-trifluoromethyl–4-nitrophenoxy)phenyl] diphenylmethane (BTFNPDM).
A mixture of **BHPP** (3.52 g, 0.01 mol), 2-chloro-5-nitrobenzotrifluoride (6.12 g, 0.02 mol), potassium carbonate (2.78 g, 0.02 mol) and *N,N*-dimethylformamide (DMF, 50 mL) was refluxed for 8 h. The mixture was cooled and poured into methanol/water (v/v=1:1) to precipitate the product. The crude product was recrystallized from DMF to provide a yellow product in 77 % yield (m.p. 227°C). The IR spectrum (KBr) exhibited absorptions at 1587 and 1335 cm^{-1} (NO_2), 1270 cm^{-1} (C-O-C). ^{1}H-NMR ($CDCl_3$): δ(ppm)= 7.00-7.04 (m, 6H); 7.22-7.24 (t, 6H); 7.27-7.29 (t, 4H); 7.32-7.35 (d, 4H); 8.28-8.31(d, 2H); 8.53-8.54 (s, 2H). ^{13}C-NMR ($CDCl_3$): δ(ppm)=64.5; 117.48; 120.93; 121.19; 121.34; 123.51; 124.15; 128.15; 129.07; 131.13; 133.36; 142.05; 144.82; 146.24; 152.44; 161.06. ANAL. calcd. for $C_{39}H_{24}O_6F_6N_2$: C, 64.11 %; H, 3.31 %; N, 3.83 %; found : C, 64.25 %; H, 3.01 %; N, 3.73 %.

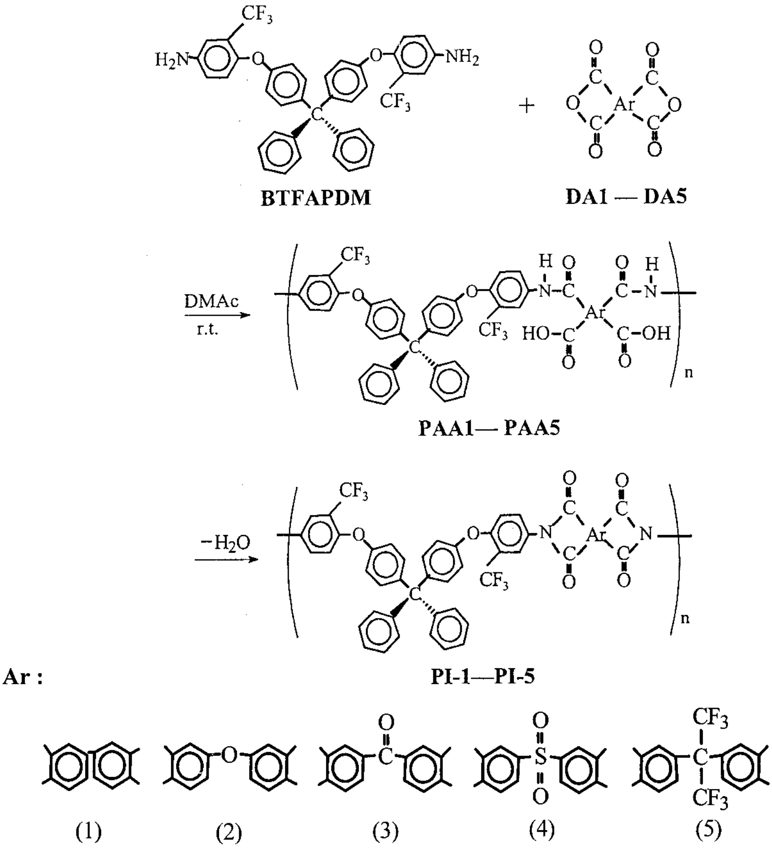
Bis[4-(2-trifluoromethyl–4-aminophenoxy)phenyl] diphenylmethane (BTFAPDM).
Hydrazine monohydrate (10 mL) was added dropwise to a mixture of **BTFNPDM** (5.4 g, 7 mmol), ethanol (40 mL), and a catalytic amount of Pd/C (0.054 g) at reflux temperature. After the addition was complete, the reaction was continued 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 and recrystallized from ethanol twice in 45 % yield (m.p. 198°C). The IR spectrum (KBr) exhibited absorptions at 3410 and 3332 cm^{-1} (N-H), 1230 cm^{-1} (C-O-C). ^{1}H-NMR ($CDCl_3$): δ(ppm)=3.71 (s, 4H); 6.73-6.75 (d, 2H); 6.82,6.84 (d, 2H); 6.87,6.89 (d, 2H); 6.93 (d, 4H); 7.13-7.28 (m, 14H). ^{13}C-NMR ($CDCl_3$): δ(ppm)=62.9; 112.95; 116.49; 119.35; 121.97; 122.75 ; 123.10; 124.69; 127.60; 131.11; 132.35; 142.57; 146.0; 146.93; 159.35. ANAL. calcd. for $C_{39}H_{28}O_2F_6N_2$: C, 69.85 %; H, 4.21 %; N, 4.18 %; found: C, 69.14 %; H, 4.40 %; N, 4.72 %.

Polymer Synthesis

To a stirred solution of **BTFAPDM** (0.6707 g, 1 mmol) in DMAc (5 mL), 4,4'-hexafluoroisopropylidenediphathalic anhydride (**DA5**) (0.4442 g, 1 mmol) was gradually added. The mixture was stirred at room temperature for 2 h under argon atmosphere to form the poly (amic acid) (**PAA5**). Chemical imidization was also carried out by adding an extra 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 heating at 100°C for 3 h. It was subsequently poured into methanol and the yellow solid precipitate was filtered off, washed with methanol and hot water, and then dried at 100°C for 24 h to afford polymer **PI-5**. All other polyimides were prepared using the similar procedure.

Measurements

Melting points were measured in capillaries on a BÜCHI apparatus (model BÜCHI 535). IR spectra were recorded in the range 4000-400 cm^{-1} for the synthesized monomers and polymers in KBr disks (JASCO IR-700 spectrometer). The inherent viscosities of all polyimides were measured using Ubbelohde viscometer. NMR spectra were recorded using a Varian VXR400S (^1H at 399.96 MHz and ^{13}C at 100.58 MHz). Thermogravimetric data were obtained on a Du Pont 2200 in flowing nitrogen (60 cm^3 min^{-1}) at a heating rate of 20°C*min^{-1}. Differential scanning calorimetry analysis was performed on differential scanning calorimeter (Du Pont 2000) at a heating rate of 20 °C*min^{-1}. Tensile properties were determined from stress-strain curves obtained with a 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 with film specimens (0.5 cm wide, 6 cm long, and ca. 0.5 mm thick). The in-plane linear coefficient of thermal expansion (CTE) was obtained from a TA TMA-2940 thermomechanical analyzer (10°C*min^{-1} from 30 to 300°C, 0.05N). The CTE value was measured on the temperature scale between 100 to 150°C. Dielectric constants were measured by the parallel–plate capacitor method using a dielectric analyzer (TA Instrumenents DEA 2970) in the frequency 1KHz on thin films. Gold electrodes were vacuum deposited on both surfaces of dried films, followed by measuring at 25°C in a sealed chamber at 0% relative humidity.



Scheme 2. Synthesis of trifluoromethyl-containing polyimides.

Results and Discussion

Preparation of Polyimides

Polyimides were prepared by the conventional two-step polymerization method, as shown in Scheme 2, involving ring-opening polyaddition forming poly (amic acid) and subsequent thermal or chemical imidization. Adding the dianhydride to the diamine solution at room temperature gave viscous poly (amic acid) solutions. The poly (amic acid) films did not break on folding/ slight manual stretching; they were thermally imidized at 300°C under vacuum to produce polyimide films. Alternatively, chemical imidization of poly (amic acid)s with a dehydrating agent such as a mixture of acetic anhydride and pyridine was also effective in obtaining polyimides. Before adding dehydrating agents, extra DMAc must be added in the poly(amic acid) solutions to prevent gelation while imidization. However, polymer **PI-1** underwent gelation on adding dehydrating agents due to their poor solubility, which is listed in Table 1. The IR spectra

Table 1. Inherent viscosity, solubility and film properties of polyimides.

Polymer	ηinh [a]	Solubility of polyimides [c]						Film
Code	(dL $\cdot$ g^{-1})	NMP	DMAc	DMF	DMSO	Pyridine	THF	Characteristics
PI-1	—[b]	-	-	-	-	-	-	—[d]
PI-2	0.65	++	++	++	+-	++	++	Very light brown to colorless, Transparent, flexible
PI-3	0.72	++	++	++	-	+	++	Very light brown to colorless Transparent, flexible
PI-4	0.58	++	++	++	+	++	++	Very light yellow to colorless, Transparent, flexible
PI-5	0.70	++	++	++	++	++	++	Very light yellow to colorless, Transparent, flexible
Ref-1	—	-	-	-	-	-	-	Light amber, flexible

a. Measured in DMAc at a concentration of 0.5 g $\cdot$ dL^{-1}at 30 °C.

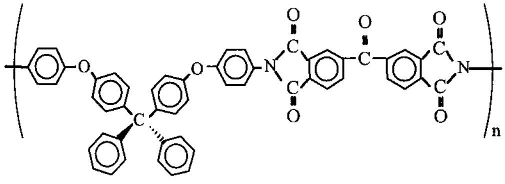
b. Polymer not soluble in DMAc.

c. Solubility: ++, soluble at room temperature; +, soluble on heating at 70°C; +-, partially soluble at 70°C; -, insoluble.

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

d. Not available.

Ref-1:



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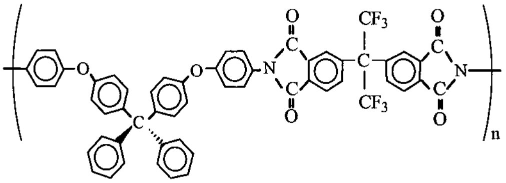

of polymers confirmed the formation of polymers. The IR spectrum of polyimide **PI-5**, obtained by chemical imidization, is shown in Figure 1. The characteristic bands at 1786

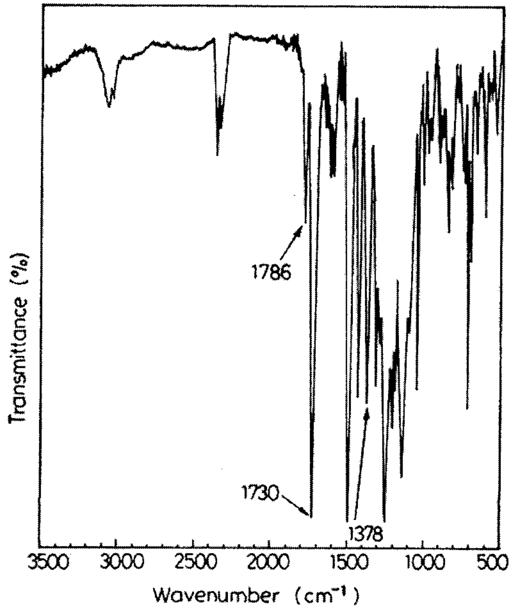

Fig. 1. IR spectrum of **PI-5**.

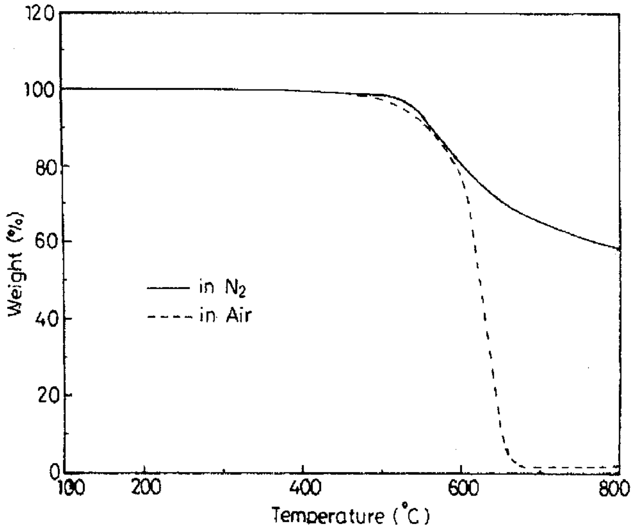

Fig. 2. TG curves of **PI-5** in nitrogen and air atmosphere at a heating rate of 20°C*min^{-1}.

and 1730 cm^{-1} are attributed to the asymmetric and symmetric stretches of imide carbonyl groups, respectively. The C-N stretching absorption at 1378 cm^{-1} confirmed the imide formation.

Polymer Properties

Solubility and film characteristics of the polyimides are listed in Table 1. The fluoro–polyimide films were very colored to almost colorless. Many non-fluorinated polyimide films are known to be yellow to dark amber on color, whereas the fluorinated polyimide films are almost colorless. Incorporation of fluorine–containing groups in the polyimide structure would reduce the refractive index and optical less. Polymers **PI-2**–**PI-5** exhibited a good solubility in a variety of solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N, N*-dimethylformamide (DMF), dimethyl sulfoxide, pyridine, and tetrahydrofuran (THF) at room temperature or upon heating at 70°C. For comparison, polyimide **Ref-1** and **Ref-2** containing diphenylmethane without trifluoromethyl were prepared by polymerizing bis[4-(4-aminophenoxy)phenyl] diphenylmethane with dianhydride **DA3** and dianhydride **DA5**. It was observed that polyimide **Ref-1** was nearly insoluble in test solvents and showed poorer solubility than its analogous polymer **PI-3**. It may be attributed to the presence of the fluorine.

Thermal properties of the polyimides are tabulated in Table 2. Glass transition temperatures of the polymers, determined by means of differential scanning calorimeter (DSC), were found to be in the range of 227-253°C. As expected the oxy-bridge containing polyimide **PI-2** had the lowest T_g.[10] The glass transition temperature of **PI-5** was higher compared to **Ref-2**. This is reasonable because fluorine atoms of the trifluoromethyl groups are bulky. The bulky trifluoromethyl groups restrict the free rotation of the polymer chains.[12] Our previous studies demonstrated a similar tendency.[11] The thermal stability of these polyimides was evaluated by thermo-gravimetric (TG) analysis. Representative TG curves of the polymer **PI-5** in nitrogen and air atmosphere are shown in Figure 2. On examining the figure the excellent stability of the polymer is apparent with a decomposition temperature in excess of 500°C in nitrogen. The decomposition temperature corresponding to 10% weight loss of these polyimides are summarized in Table 2. They reach 506-563°C and 498-557°C in nitrogen and air, respectively. Most of the polyimides suffered more weight loss in nitrogen than in air atmosphere below 600°C, indicating the high thermo-oxidative stability of the polymers. A comparison of the Td_{10} values of polymer **PI-5** and **Ref-2** revealed the higher thermal stability of the polymer with the fluorine-containing group than the polymer having no fluorine–containing unit. The residual weights in nitrogen ranged from 48-60 % at 800°C. As can be seen from Table 3 the dielectric constants of polyimides are low in general and in particular polymer **PI-5**, containing trifluoromethyl and hexafluoropropane (6F) groups was quite low. Tensile properties of the polyimide films are summarized in Table 3. The polymer films had a tensile strength of 75-87 MPa, elongation at break of 6-7 %, and tensile modulus of 1.5-2.2 GPa. Among the polymers, **PI-3** showed better tensile properties. Table 3 also shows that the CTEs of polyimides are moderate, ranging from 60-88 ppm/°C. The release of H_2O molecules during imidization process has been reported to affect the CTE of fluoropolymers.[21] In addition, we believe that the film shrinkage during imidization and the resulting possible disturbances in the molecular orientation also serious effect the CTE.

Table 2. Thermal properties of polyimides.

Polymer Code	T_g [a] (°C)	Decomposition Temperature (°C) [b]		R_{800} [c] (%)
		In N_2	In Air	
PI-1	248	553	540	59
PI-2	227	506	498	48
PI-3	247	553	537	54
PI-4	237	518	517	60
PI-5	253	563	557	60
Ref-2	239	556	552	66

a. Glass transition temperature (T_g) was measured by DSC at a heating rate of 10 °C˙ min^{-1}.

b. Temperature at which 10 % weight loss occurred, as recorded on TGA at a heating rate of 20 °C˙ min^{-1}.

c. Residual weight % at 800 °C in nitrogen.

Table 3. Physical properties of polyimide films.

Polymer Code	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)	Dielectric Constant	CTE [b] (ppm/°C)
PI-1	—[a]	—[a]	—[a]	—[a]	—[a]
PI-2	75	7	1.5	2.78	70
PI-3	87	6	2.2	2.98	60
PI-4	86	6	1.7	2.90	63
PI-5	84	7	1.5	2.46	88

a. Polymer was too brittle to be measured.

b. The CTE value was measured on the temperature scale between 100 and 150°C.

Conclusion

In this study a series of new polyimides containing diphenylmethylene unit were prepared from a new diamine bis[4-(2-trifluoromethyl-4-aminophenoxy)phenyl] diphenylmethane. Some of the polymers exhibited high solubility in common organic solvents. The polyimides showed good mechanical properties and high thermal decomposition temperature. The fluorine–containing polyimide showed a better thermal stability. Thus, the polyimides seem attractive candidates for practical applications such as processable high–temperature engineering plastics.

Acknowledgments

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