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Synthesis and characterization of novel fluorinated polyimides derived from bis[4-(4′-aminophenoxy)phenyl]-3,5-bis(trifluoromethyl)phenyl phosphine oxide

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Abstract

A novel fluorinated aromatic diamine, bis[4-(4′-aminophenoxy)phenyl]-3,5-bis(trifluoromethyl)phenyl phosphine oxide, was synthesized. A series of new fluorinated polyimides containing phosphine oxide was prepared from the novel diamine with various commercially available aromatic dianhydrides. All the fluorinated polyimides show high glass transition temperatures, excellent thermal stability, and good solubility in common organic solvents.

Keywords: Phenylphosphine oxide; Fluorinated polyimide; Thermally stable polymer

1. Introduction

Aromatic polyimides (PIs) have been widely used in high temperature films, adhesives, molded parts and microelectronic encapsulation, aviation and separation for the past few decades due to their excellent thermal stability, mechanical strength, low dielectric constants, adhesive and mechanical properties, chemical resistance, and dimensional stability [1–4]. However, some applications are often limited by the poor solubility and high processing temperature partly due to rigid polymer backbones and the strong interchain interaction. Many attempts have been made to improve the processability of polyimides without sacrificing their thermal and mechanical properties. During the past decades, some progress has been made in the chemical modification of the parent polyimide structure to get more soluble polymer derivatives, for example, introducing the flexible linkages or geometrically asymmetric units, bulky lateral groups or noncoplanar structures into the polymer backbone, the use of monomers and oligomers endcapped with reactive groups, as well as designing fluorine-containing monomer and polymer chain [5–11].

The fluorination of polyimides, which Critchley et al. [12] pioneered, has received much attention because of the improvement of the physical, dielectric and optical properties of polyimides [13]. Thus fluorinated aromatic polyimides, especially trifluoromethyl-containing polyimides [14], have been identified as one of the important polyimide materials. The bulky trifluoromethyl groups can inhibit efficiently the PI to form regular chain structure and increase the molecular polarity correspondingly, therefore, the resulting polyimide molecule tends to contain a high free volume, thus exhibits a good solubility in organic solvents without sacrificing the above excellent properties. Recent studies demonstrated that polyimides derived from ether-bridged aromatic diamines with trifluoromethyl groups exhibit some excellent physical

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properties, such as high solubility with low moisture uptake, low dielectric constant, high optical transparency, and low birefringence [15,16]. Though the fluorination of polyimides shows some desirable properties, this kind of polyimide still has some drawbacks, such as poor adhesion, low glass transition temperatures (T_g), and high coefficients of thermal expansion (CTEs) [17].

Polymers containing the phenylphosphine oxide (PPO) group have been studied extensively for a number of applications in recent years. These polymers are also known to exhibit excellent adhesion properties to metal substrates [18] and miscibility with many thermoplastic and thermosetting polymers. Due to the noncoplanar structure of triarylphosphine oxide and the intensely polar P═O bond, polymers containing the PPO group are usually amorphous [18], have low birefringence [19] and high refractive index [20]. The incorporation of the triarylphosphine oxide moiety into the backbone of aromatic polymers not only increases the solubility of the polymer in common organic solvents [21], but also improves the nonlinear optical properties of polymers due to the excellent electron-accepting ability of the PPO group [22]. A notable feature of the PPO is resistance to atomic oxygen (AO) has received considerable interest. Connell and co-workers at NASA Langley have developed a series of PPO containing polymers for durability in space environments [23]. Polymers derived from triphenylphosphine oxide have been suggested for a number of applications such as coatings for low earth orbit application [24], heat shields [23], thermal blankets [23], and oxygen plasma etch barriers [25].

Therefore, in an attempt to combine these features in a polyimide a novel aromatic diamine containing phosphine oxide and trifluoromethyl groups, bis[4-(4′-aminophenoxy)phenyl]-3,5-bis(trifluoromethyl)phenyl phosphine oxide **4**, was designed and synthesized in our laboratory, and a series of novel fluorinated aromatic polyimides were prepared by polycondensation of **4** with various commercially available aromatic dianhydrides. The solubility of the resulting polyimides in several common organic solvents was observed. The polycondensation process, corresponding composition and structure, as well as physical, thermal and optic properties of the polymers were investigated.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) was freshly distilled under nitrogen over sodium. Pyridine was distilled over calcium hydride. *N*-Methylpyrrolidinone (NMP) was stirred over phosphorus pentoxide overnight at room temperature, and then vacuum-distilled. 4-Bromo-1-fluorobenzene, diethyl phosphite, 3,5-bis(trifluoromethyl)bromobenzene and thionyl chloride were distilled prior to use. Magnesium turnings were treated with 5% aqueous hydrochloric acid for several minutes, and then washed with water, ethanol and ether, respectively, and dried in vacuum. Other reagents or materials were used as received.

2.2. Measurements

Melting point ranges were determined on a WRS-2A capillary melting point apparatus (uncorrected). Elemental analysis was carried out on a Carlo-Erba1106 system. Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Gas chromatography/mass spectrometry (GC/MS) was recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker AM 400 spectrometer system. Chloroform-*d* and dimethyl sulphoxide-d_6 were used as the solvents and chemical shifts reported were internally referenced to Me_4Si (0 ppm), $CFCl_3$ (0 ppm) and H_2PO_3 for ^{1}H, ^{19}F and ^{31}P nuclei, respectively. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual-wavelength absorbance detector and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8 × 300 mm). GPC measurements were carried out at 35 °C using THF as eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was conducted on a NetZSch (German) DSC 204 F1 system under nitrogen calibrated with indium and zinc standards. Initial sample weight was set as 2–4 mg for each operation. The specimen was heated from 50 to 300 °C at a heating rate of 10 °C/min. Dynamic thermo-gravimetric analysis (TGA) was performed on NetZSch (German) TGA 209 F1 system on film or powder samples at a heating rate of 10 °C/min under nitrogen atmosphere from 25 to 760 °C. Ultraviolet–visible (UV–vis) spectra were recorded on a Lambda 35 (Perkin Elmer) spectrophotometer. The wide-angle X-ray diffraction (XRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu/Kα1 radiation, operated at 40 kV and 300 mA. Inherent viscosities were measured with an Ubbelohde viscometer with 5 wt% of NMP solution at 25 °C. Water uptakes were determined by weighing the changes of polyimide film ($50 \times 50 \times 0.05$ mm^3) before and after immersion in water at 25 °C for 24 h. The solubility was determined by immersing 1.0 g polyimide in various solvents (10.0 g) at 25 °C with magnetic stirring for 24 h.

*2.3. Synthesis of bis(4-fluorophenyl)phosphinic acid **1***

The synthesis of bis(4-fluorophenyl)phosphinic acid has been previously described [26].

*2.4. Synthesis of bis(4-fluorophenyl)phosphinic chloride **2***

Compound **1** (50.8 g, 0.2 mol) was dissolved in 200 mL of thionyl chloride and stirred at 55 °C for 2 h. The mixture was warmed to 80 °C to remove excess thionyl chloride. The trace quantities of thionyl chloride were removed in vacuum. The product was immediately used without further isolation or purification. ^{1}H NMR ($CDCl_3$, ppm): δ 7.73 (m, 4H), 7.09 (m, 4H). ^{19}F NMR ($CDCl_3$, ppm): δ −105.7 (m, 2F).

*2.5. Synthesis of bis(4-fluorophenyl)-3,5-bis(trifluoromethyl)-phenylphosphine oxide **3***

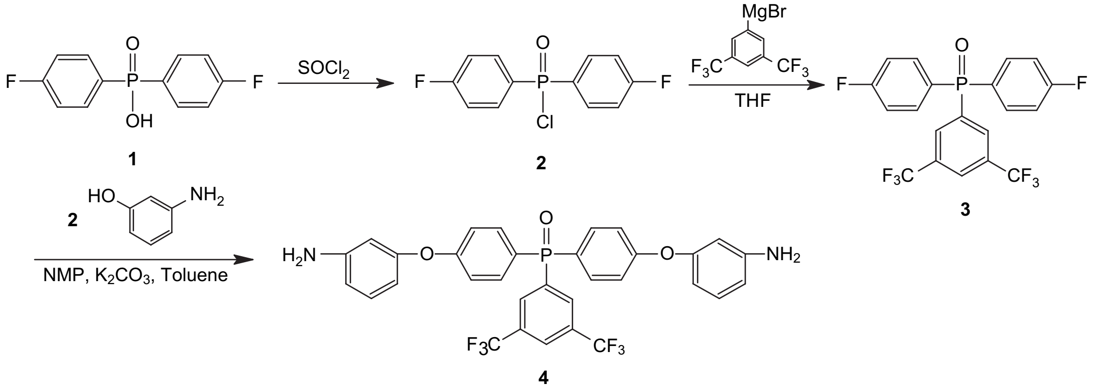
Compound **3** was synthesized via the Grignard reaction (Scheme 1). Mg turnings (6.0 g, 0.25 mol) and THF (200 mL) were added to a flame-dried 1 L four-neck round-bottom flask, equipped with a mechanical stirrer, a dropping funnel, a thermometer and a condenser with a drying tube. The solution was cooled to below 5 °C with ice bath, then a solution of 3,5-bis(trifluoromethyl)bromobenzene (72.8 g, 0.25 mol) in THF (100 mL) was added dropwise while the temperature was kept below 5 °C. After the addition was complete, the mixture was allowed to slowly warm to room temperature and stirred for 24 h, and the flask was subsequently placed in an ice-water bath to cool the mixture to about 5 °C. A solution of **2** in THF (100 mL) was added dropwise while the temperature was kept below 5 °C. After addition was complete, the mixture was allowed to slowly warm to room temperature and stirred for 24 h. The resulting brown solution was poured into a mixture of 10% sulfuric acid solution (200 mL) and water (300 mL) to give two layers. The organic layer was isolated and washed successively with water, 5% aqueous sodium bicarbonate and water, then dried over magnesium sulfate. The solvent was removed to give a dark red viscous liquid (82.8 g, 92% crude yield). The crude product was vacuum-distilled (at ~20 mm Hg) from 170 to 174 °C, and a yellow semisolid was collected (72 g, 80% yield). The solid was recrystallized twice from cyclohexane with charcoal and Celite treatment to afford **3** (58.5 g, 65% yield) as white solid: mp 121.7–122.5 °C. IR (KBr, cm^{-1}): 1197 (P=O). ^{1}H NMR ($CDCl_3$, ppm): δ 8.10 (s, 1H), 8.07 (s, 1H), δ 8.04 (s, 1H), 7.59 (m, 4H), 7.17 (q, $J=7.25$ Hz, 4H). ^{19}F NMR ($CDCl_3$, ppm): δ −62.9 (s, 6F), −104.2 (t, $J_{HF}=7.52$ Hz, 2F). ^{31}P NMR ($CDCl_3$, ppm): δ 25.5 (s). MS (EI): *m/z* 450, 431. Anal. Calcd for $C_{20}H_{11}F_8OP$: C, 53.33%; H, 2.44%. Found: C, 53.19%; H, 2.74%.

*2.6. Synthesis of bis[4-(4′-aminophenoxy)phenyl]-3,5-bis(trifluoromethyl)phenyl phosphine oxide **4***

To a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, and a Dean–Stark trap were added **3** (36 g, 0.08 mol), 3-aminophenol (18.5 g, 0.17 mol), potassium carbonate (29.0 g, 0.21 mol), NMP (150 mL) and toluene (80 mL). The mixture was heated with stirring to 135 °C while removing water via azeotropic distillation. After 24 h, toluene was removed from the reaction, and the resulting solution was heated to 160 °C and continued stirring for 8 h at 160 °C. The reaction mixture was cooled to room temperature and then poured into 500 mL of 5% aqueous acetic acid with vigorous stirring. A tan gum formed that eventually solidified with stirring. The crude solid was collected via filtration, washed with excess water, and dried at 110 °C to afford 42.7 g of **4** (85%). The solid was recrystallized twice from ethanol with charcoal and Celite treatment to afford **4** (30.1 g, 60% yield) as white solid: mp 193.6–194.2 °C. IR (KBr, cm^{-1}): 3450, 3340, 3223 (N–H), 1175 (P=O). ^{1}H NMR ($CDCl_3$, ppm): δ 8.07 (d, 2H), 7.96 (s, 1H), 7.50 (q, $J=8.70$ Hz, 4H), 7.07 (t, $J=8.06$ Hz, 2H), 7.00 (q, $J=2.26$ Hz, 4H), 6.45 (q, 2H), 6.38 (q, 2H), 6.32 (t, $J=2.01$ Hz, 2H), 3.26 (br, 4H). ^{19}F NMR ($CDCl_3$, ppm): δ −62.8 (s, 6F). ^{31}P NMR ($CDCl_3$, ppm): δ 26.6 (s). MS (EI): *m/z* 628. Anal. Calcd for $C_{32}H_{23}N_2F_6O_3P$: C, 61.15%; H, 3.66%; N, 4.46%. Found: C, 61.26%; H, 3.91%; N, 4.24%.

2.7. General polymerization procedure

Phenylphosphine oxide-containing polyimides were prepared from the reaction of stoichiometric quantities of **4** with various aromatic dianhydrides under a nitrogen atmosphere. The following procedure is for the preparation of **PI-1** and is representative for the preparation of all polymers. Into a 100 mL three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube filled with calcium sulfate were placed **4** (3.125 g, 5.0 mmol) and NMP (8.0 mL). Once dissolved, oxydiphthalic dianhydride (1.550 g, 5.0 mmol) was added with additional NMP (10.0 mL) to give a solution with a concentration of 20% (w/w) solids. The resulting light yellow solution was stirred for 24 h at room temperature under a nitrogen atmosphere. The remaining polymer solution was chemically imidized by the addition of 1.54 g of acetic anhydride and 1.19 g of pyridine. The solution was stirred at room temperature for 24 h. The polymer was precipitated in a blender containing a 50/50 (v/v) mixture of water/methanol, filtered, washed successively with excess water and



Scheme 1. Synthesis of compound **4**.

methanol, and then dried in a vacuum oven at 110 °C overnight to afford a white, fibrous material.

PI-1 (**4**/ODPA): IR (KBr, cm^{-1}): 1783, 1727, 1180 (P=O). ^1H NMR (DMSO-d_6, ppm): δ 8.44 (s, 1H), 8.26 (d, 2H), 8.09 (d, 2H), 7.79 (t, 4H), 7.63 (q, 6H), 7.37 (d, 2H), 7.27 (d, 8H). ^{19}F NMR (DMSO-d_6, ppm): δ −61.3 (d, 6F). ^{31}P NMR (DMSO-d_6, ppm): δ 23.3 (s). Anal. Calcd for $C_{48}H_{25}N_2F_6O_8P$: C, 63.86%; H, 2.77%; N, 3.10%. Found: C, 63.13%; H, 3.01%; N, 2.99%.

PI-2 (**4**/PMDA): IR (KBr, cm^{-1}): 1780, 1729, 1174 (P=O). ^1H NMR (DMSO-d_6, ppm): δ 8.29 (s, 1H), 8.21 (d, 2H), 8.12 (d, 2H), 7.64 (t, 4H), 7.49 (t, 2H), 7.26 (d, 2H), 7.19 (s, 2H), 7.10 (d, 6H). ^{19}F NMR (DMSO-d_6, ppm): δ −61.3 (d, 6F). ^{31}P NMR (DMSO-d_6, ppm): δ 23.3 (s). Anal. Calcd for $C_{42}H_{21}N_2F_6O_7P$: C, 62.22%; H, 2.59%; N, 3.46%. Found: C, 61.18%; H, 2.81%; N, 3.16%.

PI-3 (**4**/BTDA): IR (KBr, cm^{-1}): 1785, 1735, 1725, 1681, 1183 (P=O). ^1H NMR (DMSO-d_6, ppm): δ 8.47 (s, 1H), 8.28 (d, 4H), 8.17 (d, 4H), 7.81 (t, 4H), 7.65 (d, 2H), 7.40 (d, 2H), 7.31 (d, 8H). ^{19}F NMR (DMSO-d_6, ppm): δ −61.3 (s, 6F). ^{31}P NMR (DMSO-d_6, ppm): δ 23.3 (s). Anal. Calcd for $C_{49}H_{25}N_2F_6O_8P$: C, 64.33%; H, 2.74%; N, 3.06%. Found: C, 63.58%; H, 2.90%; N, 2.73%.

PI-4 (**4**/s-BPDA): IR (KBr, cm^{-1}): 1782, 1730, 1183 (P=O). ^1H NMR (DMSO-d_6, ppm): δ 8.47 (s, 1H), 8.24 (d, 4H), 8.04 (d, 4H), 7.77 (t, 4H), 7.62 (d, 2H), 7.34 (d, 2H), 7.23 (d, 8H). ^{19}F NMR (DMSO-d_6, ppm): δ −61.3 (s, 6F). ^{31}P NMR (DMSO-d_6, ppm): δ 23.3 (s). Anal. Calcd for $C_{48}H_{25}N_2F_6O_7P$: C, 65.01%; H, 2.82%; N, 3.16%. Found: C, 64.51%; H, 3.03%; N, 2.78%.

2.8. Film preparation

Thin films were cast from polyimide solutions in NMP, or chloroform (typically 10–15% w/w solids). The polymer solutions were centrifuged, and the decantate was coated onto clean, dry plate glass and dried to a tack-free form in a low-humidity chamber. The films were then stage-dried in a forced air oven at 50 °C for 2 h, 100 °C for 1 h, 150 °C for 1 h, and 200 °C for 1 h.

3. Results and discussion

3.1. Synthesis of diamine 4

This novel diamine was synthesized in three steps as shown in Scheme 1. In the first step bis(4-fluorophenyl)phosphinic acid was converted into bis(4-fluorophenyl)phosphinic chloride **2** with thionyl chloride. Since **2** readily hydrolyzes to bis(4-fluorophenyl)phosphinic acid in air, it was prepared and immediately used without further isolation or purification. The second step involved a Grignard reaction between 3,5-bis(trifluoromethyl)bromobenzene (25% molar excess) and bis(4-fluorophenyl)phosphinic chloride **2**. The crude product was obtained in 80% yield. Initial purification of this material was difficult since phosphine oxide compounds, in general, are soluble in many organic solvents, and purification via crystallization is often difficult. Purification of the crude Grignard product **3**, typically obtained as viscous red oil after reaction, was accomplished by vacuum distillation to give a light yellow semisolid. The semisolid was subsequently crystallized from cyclohexane to afford a white crystalline solid in 65% overall yield. Compound **3** was subsequently reacted with 2.1 equiv. of 3-aminophenol in the presence of potassium carbonate in NMP to yield **4**. Two recrystallizations of diamine **4** from ethanol afforded polymer grade monomer in 60% overall yield.

The composition and structure of diamine **4** were confirmed by MS, FT-IR, ^1H NMR, ^{19}F NMR, ^{31}P NMR and elemental analysis. In the IR spectra of **3** and **4**, the C–F multiple stretch bending absorptions from trifluoromethyl group were observed between 1400 and 1000 cm^{-1} (Fig. 2). For **4**, the P=O stretching absorption appeared at 1175 cm^{-1}. In addition, **4** showed typical N–H stretching absorptions at 3450, 3340 and 3223 cm^{-1}, N–H bending absorption at 780 cm^{-1} due to the amine groups compared to **3**. This indicated that compound **3** completely converted into compound **4**. From the ^1H NMR spectrum (Fig. 1A) of **4**, it can be seen that protons in 3,5-bis(trifluoromethyl)phenyl pendant group appeared at 8.07 ppm (d, H_2, 2H) and 7.96 ppm (s, H_1, 1H); signals of 7.50 (m, H_3, 4H) and 7.00 (q, H_4, 4H) belonged to protons in diphenylphosphine oxide moiety; 7.07 (t, H_5, 2H), 6.45 (q, H_6, 2H), 6.38 (q, H_8, 2H), and 6.32 (t, H_7, $J_{6,7} = 2.01$ Hz, 2H) belonged to protons in amino phenyl moieties; and 3.26 ppm (br, 4H) for protons in amino groups. In ^{19}F NMR spectrum, fluorines in 3,5-bis(trifluoromethyl)phenyl moiety appeared at −62.8 ppm (s, 6F) for **4** (Fig. 1B). ^{31}P NMR spectrum provided a triplet peak at 26.6 ppm for **4** (Fig. 1C). Further characterization of **4** by elemental analysis provided experimental result, which was matched to the theoretical values, confirming the successful synthesis of the high-purity monomer.

3.2. Polymer synthesis

Polyimides containing PPO groups were prepared from **4** and various aromatic dianhydrides in NMP under a nitrogen atmosphere as shown in Scheme 2. Typically, the poly(amide acid) was prepared by the addition of a molar equiv. of dianhydride as a solid to a solution of diamine dissolved in solvent. Solvent was then added to form a 20% (w/w) solution. The reaction mixture was stirred at room temperature for 24 h followed by chemical imidization/cyclodehydration using a mixture of acetic anhydride and pyridine. The resulting polymers were isolated in >90% yield.

The polyimides derived from **4** and aromatic dianhydrides were viscous with inherent viscosities determined in NMP at 25 °C in the range of 0.42–1.01 dL/g (Table 1). This indicated medium to high molecular weight polymer formation. The chemical structures of PIs were characterized by FT-IR, ^1H NMR, ^{19}F NMR and ^{31}P NMR, and element analysis. All of the polyimides showed characteristic imide absorption bands at 1780–1785 cm^{-1} and 1727–1735 cm^{-1}. The peak at 1780–1785 cm^{-1} was attributable to the asymmetrical carbonyl stretching vibrations, and that at 1727–1735 cm^{-1} to

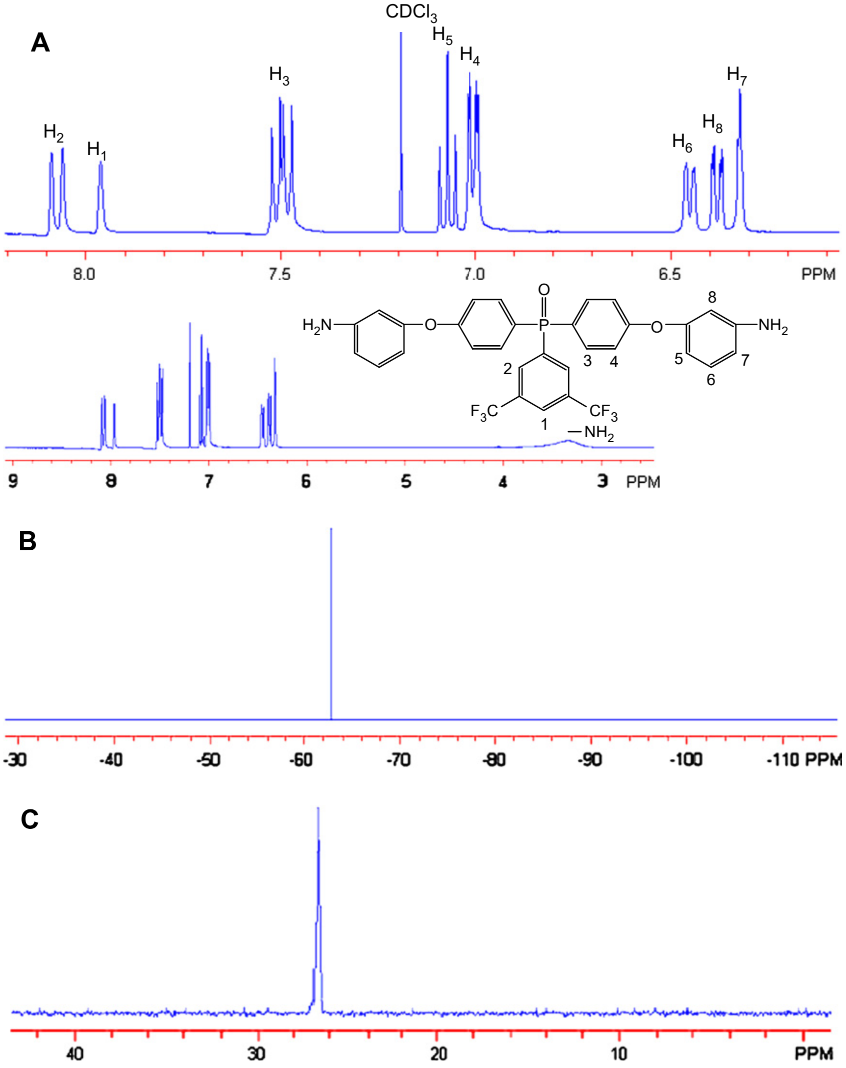


Fig. 1. ^{1}H NMR (A), ^{19}F NMR (B) and ^{31}P NMR (C) spectra of compound **4**.

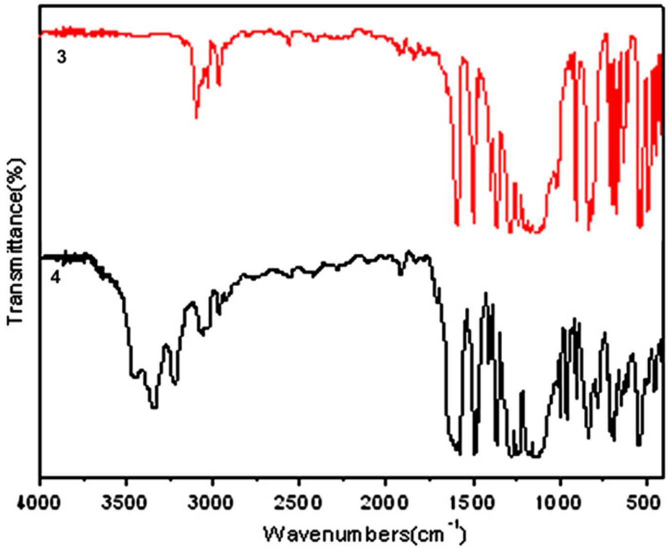
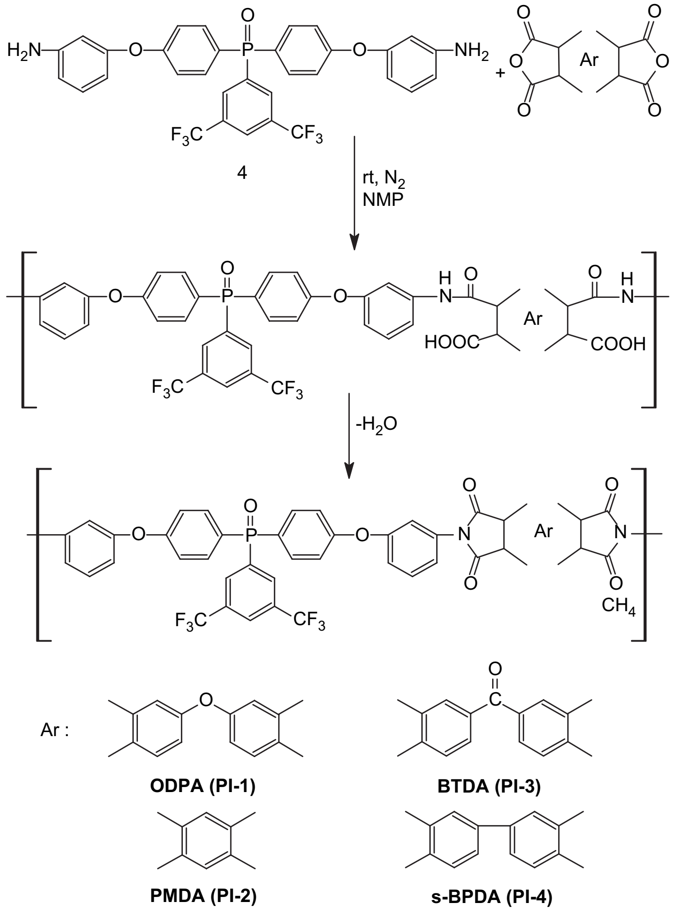


Fig. 2. FT-IR spectra of **3** and **4**.

the symmetrical carbonyl stretching vibrations (Fig. 3). The absorption at 1380 cm^{-1} was assigned to C–N stretching, and the C–F multiple stretching absorptions were also detected in the range of 1300–1100 cm^{-1}. Fig. 4 depicts typical ^{1}H, ^{19}F and ^{31}P NMR spectra of the aromatic fluorinated polyimide **PI-1** which confirmed the chemical structure of **PI-1**. The element analysis data for fluorinated polyimides are in good agreement with the calculated values for the proposed chemical structures. The molecular weights of the fluorinated polyimides determined by GPC in THF using polystyrene as standard are in the range of 31 520–75 950 for M_n and 46 960–82 790 for M_w with the M_w/M_n values of 1.1–1.5 (Table 1). This narrow molecular weight distribution was similar to what some researchers [27] reported (the M_w/M_n values about 1.5).

3.3. Polymer solubility

Table 2 shows solubility of the fluorinated polyimides determined quantitatively by dissolving 1.0 g of solid polyimide



Scheme 2. Synthesis of phenylphosphine oxide-containing fluorinated polyimides.

Table 1
Physical properties of the fluorinated polyimides

Polymers	Dianhydride	Color	η_{inh}[a](dL/g)	M_n[b]	M_w[b]	(M_w/M_n)[b]
PI-1	ODPA	Colorless	0.68	46 900	58 780	1.3
PI-2	PMDA	Yellow	0.46	34 480	48 570	1.4
PI-3	s-BPDA	Colorless	1.01	75 950	82 790	1.1
PI-4	BTDA	Yellow	0.42	31 520	46 960	1.5

[a] η_{inh} at 5 wt% of polyimides in NMP at 25 °C.
[b] GPC in THF vs. polystyrene at 35 °C.

in 10.0 g of organic solvents. It can be seen that the phenylphosphine oxide-containing fluorinated polyimides showed good solubility in common organic solvents, such as NMP, DMAc, DMSO, DMF, THF, chloroform and dioxane. The good solubility could be resulted from the presence of PPO group, the introduction of flexible links (*meta*-ether linkage) and bulky trifluoromethyl groups [28]. It should be noted that the good solubility in common low boiling point solvent is useful to prepare polyimide films or coating at relatively low processing temperature, which is desirable for advanced applications.

The WAXD patterns of the fluorinated polyimides are shown in Fig. 5. They showed that all of the polymers were amorphous. No crystalline or semi-crystalline phase was detected. This might be interpreted by the presence of bulky trifluoromethyl-substituted phenyl groups, which decreased the intra- and inter-polymer chain interactions, resulting in loose polymer chain packaging and aggregates. The amorphous phase endows some special features to polyimide, such as good solubility in solvents.

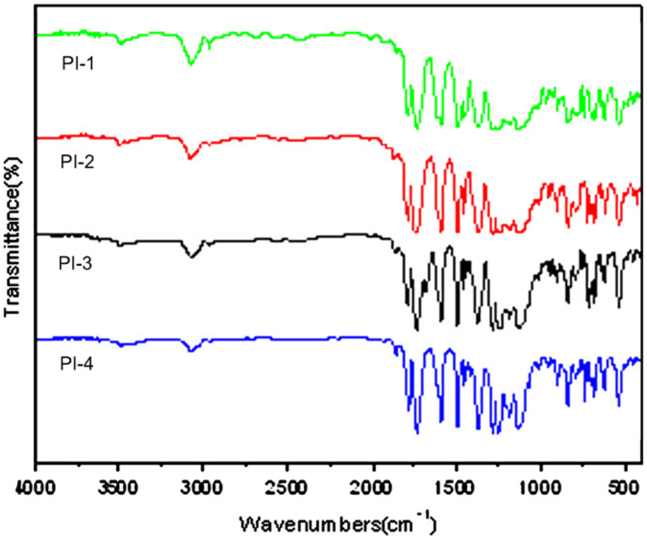


Fig. 3. FT-IR spectra of the fluorinated polyimides.

3.4. Thermal properties of polymers

Thermal properties of the polyimides were evaluated by means of differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA). The results are listed in Table 3. DSC was used to determine the glass transition temperature values of the polyimides with a heating rate of 10 °C/min in nitrogen. Fig. 6 compares the DSC curves of the polyimide series. The T_g's ranged from 200 to 232 °C. As expected, **PI-2** derived from the relatively rigid PMDA exhibited the highest T_g (232 °C), 32 °C higher than **PI-1** derived from the most flexible ODPA (200 °C). This result is well correlated to the stiffness/bulkiness of dianhydride moieties (PMDA>s-BPDA>BTDA>ODPA) [29]. Fig. 7 shows TGA curves of the fluorinated polyimides under nitrogen atmosphere. A slight weight loss before 400 °C in TGA curves could be due to trace quantities of solvent such as NMP in polyimides or the instability of the instrument which resulted in the fluctuation of the baseline. The polymers exhibited temperatures corresponding to 5% weight loss ranging from 441 to 487 °C under nitrogen, and the initial thermal decomposition temperatures (T_d) were determined in the range of 529–546 °C in nitrogen and 512–538 °C in air for all polyimides tested. As expected, the polymers exhibited significantly higher stability in nitrogen than in air, as shown in Table 3 the weight loss appeared to start at lower temperature. Meanwhile, the anaerobic char yield at 760 °C is also summarized in Table 3. The char yields of the fluorinated polyimides at 760 °C under nitrogen are 48.5–55.5%. The high residue

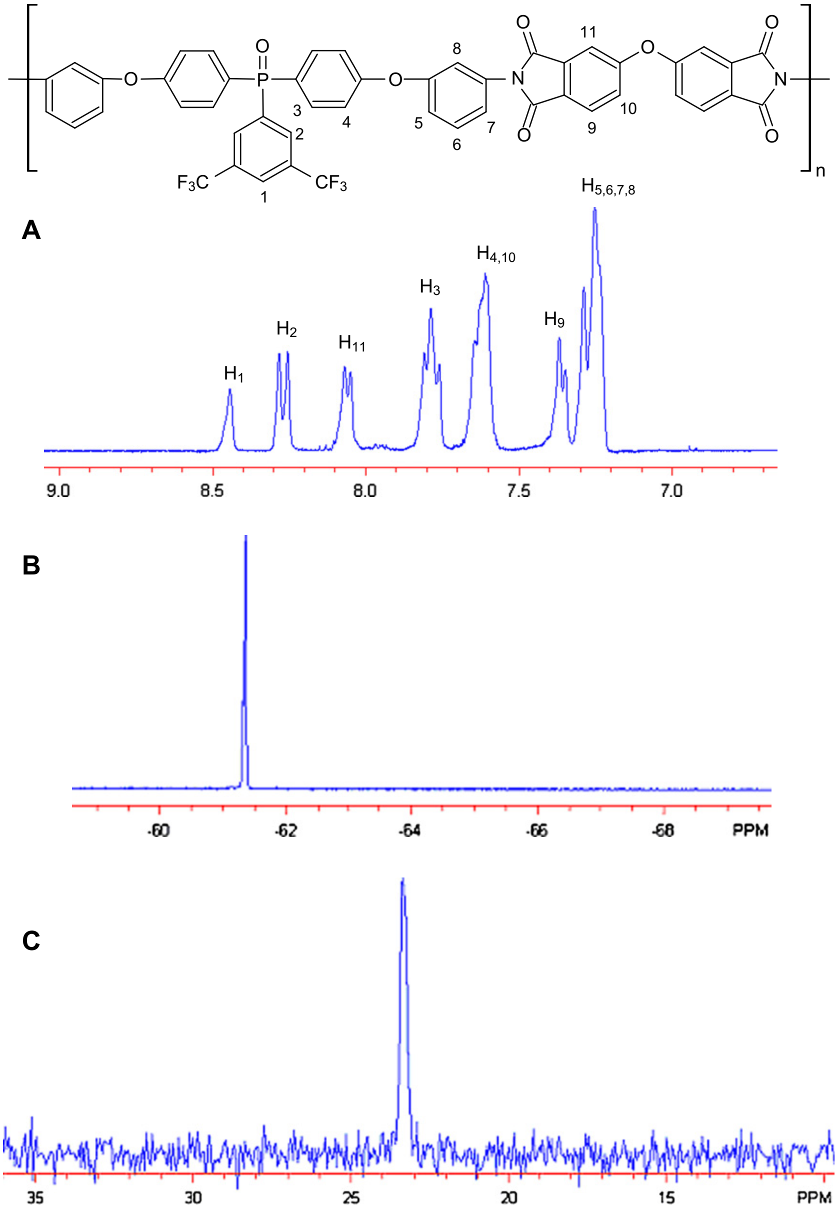


Fig. 4. ^1H NMR (A), ^{19}F NMR (B) and ^{31}P NMR (C) spectra of **PI-1**.

Table 2
Solubility of the fluorinated polyimides[a]

	DMF	NMP	DMAc	$CHCl_3$	Dioxane	THF	Acetone	Toluene
PI-1	S	S	S	S	S	S	S	P
PI-2	S	S	S	S	S	S	P	I
PI-3	S	S	S	S	S	S	S	P
PI-4	S	S	S	S	S	S	P	I

[a] At 25 °C for 24 h, S: soluble; P: partially soluble; I: insoluble.

at 760 °C under an atmosphere of nitrogen is attributed to the presence of phosphine oxide and the presence of fluorine in polyimide [14c,19b]. The results of thermal analysis demonstrate that the resulting polyimides should hold excellent thermal stability, which would be facilitated to their application.

3.5. Optical properties

Fig. 8 shows the UV–vis spectra of the fluorinated polyimide films with thickness of 30 μm, in which the cutoff wavelength ranged from 350 to 370 nm and the transmittance in visible region was 70–80%. **PI-3** showed a cutoff wavelength at 350 nm, 17 nm lower than **PI-2**, while **PI-2** had the highest fluorine content in the polyimide backbone (14.1%, Table 3). It could be attributed to the color in the film of **PI-2**. Meanwhile, biphenyl group of s-BPDA existing in **PI-2** backbone could form π-bond and result in the color of the film. Diamine **4** contains PPO group, *meta*-linkage and a bulky pendant group and thus provides a highly irregular structure to the polyimide. This was expected to disrupt the formation of charge transfer complexes and lead to low color polyimide films. Depending on the dianhydride used, virtually colorless polyimide

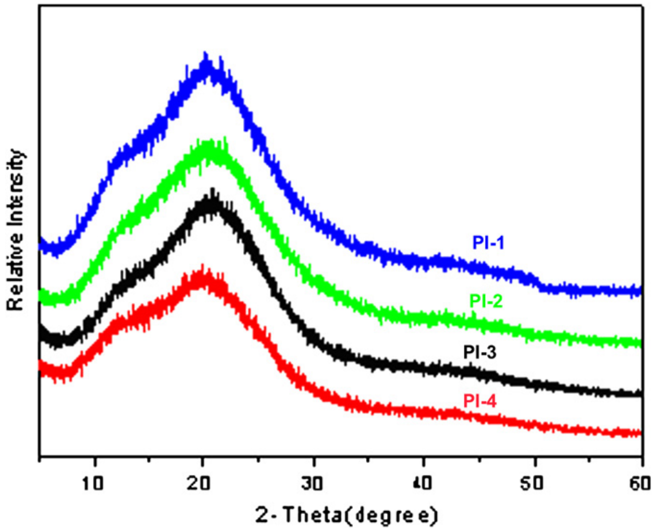


Fig. 5. Wide-angle X-ray diffraction patterns of the polyimide films.

films were prepared (Table 2). **PI-1** and **PI-3** were nearly colorless. **PI-2** and **PI-4** were light yellow.

The fluorinated polyimides also showed very low water uptakes in the range of 1.12–1.60% (Table 3). **PI-2** exhibited the lowest water uptake value (1.12%), compared to **PI-3** (1.60%). Apparently, the low water uptakes were mainly attributed to the polymer hydrophobicity derived from the rigid backbone structure and the fluorine density.

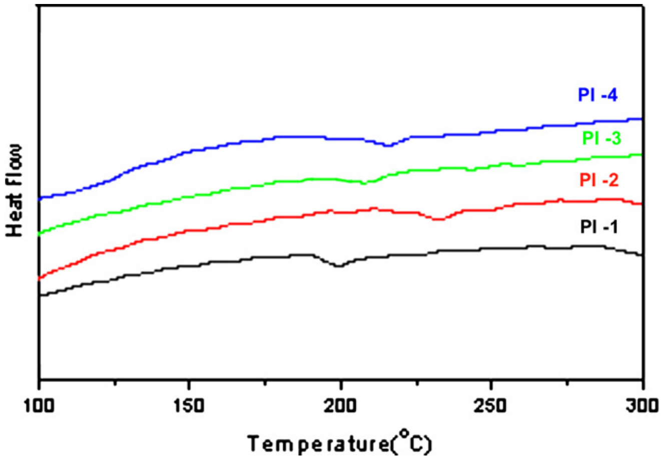


Fig. 6. DSC curves of the fluorinated polyimides.

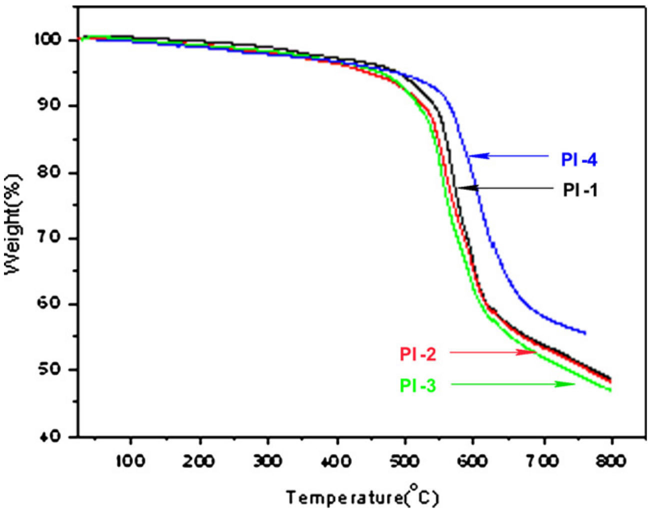


Fig. 7. TGA curves of the fluorinated polyimides in nitrogen.

4. Conclusion

A novel diamine, bis[4-(4′-aminophenoxy)phenyl]-3,5-bis(trifluoromethyl)phenyl phosphine oxide, was prepared, characterized, and subsequently reacted with various aromatic dianhydrides to prepare phenylphosphine oxide-containing fluorinated polyimides. The PPO group, bulky trifluoromethyl

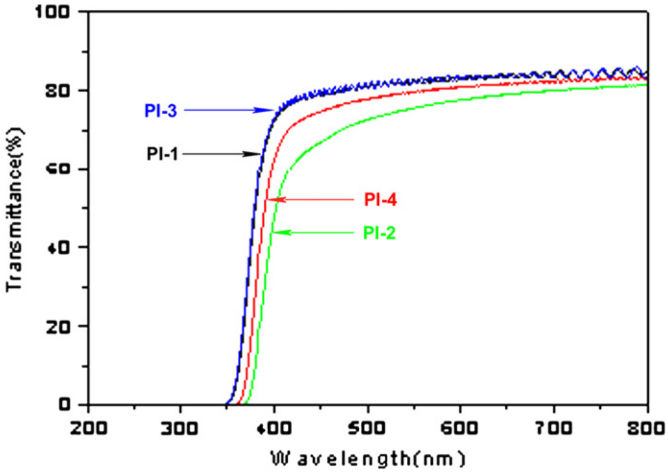


Fig. 8. UV–visible spectra of the polyimide films (thickness = 30 μm).

Table 3
Thermal and optical properties of the fluorinated polyimides

Polymers	F[a] (%)	T_g[b] (°C)	T_d[b] (°C)		5% Weight loss in N_2	Char yield[c] (%) in N_2	λ_{cut}[d] (nm)	W_u[e] (%)
			In air	In N_2				
PI-1	12.6	200	538	544	485	50.5	350	1.53
PI-2	14.1	232	530	534	441	50.1	370	1.12
PI-3	12.5	207	523	529	462	48.5	353	1.60
PI-4	12.9	215	512	546	487	55.5	364	1.34

[a] Fluorine contents.
[b] DSC and TGA at 10 °C/min in N_2.
[c] Residual weight retention at 760 °C.
[d] Cutoff wavelength.
[e] Water uptakes.

groups and *meta*-linkages serve to increase the solubility of the fully imidized polymers. The bulky trifluoromethyl pendant to the polymer backbone is not only responsible for enhancing the solubility but also is partially responsible for imparting low color to the films by reducing charge transfer complex formation. Meanwhile, the resulting polyimides have high glass transition temperatures, excellent thermal stability, good spectral transmittances, and low water uptakes.

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References

[1] Mittal KL, editor. Polyimide: synthesis, characterization, and application. New York: Plenum Press; 1984. p. 1102.

[2] Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. London: Blackie Glasgow; 1990. p. 1–30.

[3] Kricheldorf HR, editor. Progress in polyimide chemistry I. Berlin: Springer; 1990. p. 10.

[4] (a) Leng WN, Zhou YM, Xu QH, Liu JZ. Polymer 2001;42:9253–9;
(b) Einsla BR, Kim YS, Hicker MA, Hong YT, Hill ML, Pivovar BS, et al. J Membr Sci 2005;255:141–8;
(c) Einsla BR, Hong YT, Kim YS, Feng W, Gunduz N, McGrath JE. J Polym Sci Part A Polym Chem 2004;42(4):862–74.

[5] (a) Zhou HW, Liu JG, Qian ZG, Zhang SY, Yang SY. J Polym Sci Part A Polym Chem 2001;39:2404–13;
(b) Sasthav JR, Harris FW. Polymer 1995;36(26):4911–7.

[6] Liaw DJ, Hsu PN, Chen WH, Liaw BY. J Polym Sci Part A Polym Chem 2001;39:3498–504.

[7] Yamashita M, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem 1993;31:1513–8.

[8] Liou GS, Hsiao SH, Ishida M, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem 2002;40:2810–8.

[9] Reyx D, Campistron I, Caillaud C, Villatte M, Cavedon A. Macromol Chem Phys 1995;196:775–85.

[10] (a) Yang CP, Wei CS. Polymer 2001;42:1837–48;
(b) Qian ZG, Ge ZY, Li ZX, He MH, Liu JG, Pang ZZ, et al. Polymer 2002;43:6057–63.

[11] Choi WS, Harris FW. Polymer 2000;41(16):6213–21.

[12] Critchley JP, Grattan PA, Whitte MA, Pippett JS. J Polym Sci Part A Polym Chem 1972;10:1789–807.

[13] (a) Bes L, Rousseau A, Boutevin B, Mercier R. J Polym Sci Part A Polym Chem 2001;39:2602–19;
(b) Takahsaki T, Kuwana Y, Takahashi T, Hayashida S. J Polym Sci Part A Polym Chem 2000;38:4832–8.

[14] (a) Yang CP, Su YY. Polymer 2005;46:5797–807;
(b) Yin DX, Li YF, Yang HX, Yang SY, Fan L, Liu JG. Polymer 2005;46:3119–27;
(c) Li HS, Liu JG, Wang K, Fan L, Yang SY. Polymer 2006;47:1443–50.

[15] (a) Xie K, Liu JG, Zhou HW, Zhang SY, He MH, Yang SY. Polymer 2001;42:7267–74;
(b) Liu JG, He MH, Li ZX, Qian ZG, Wang FS, Yang SY. J Polym Sci Part A Polym Chem 2002;40:1572–82.

[16] (a) Yang CP, Hsiao SH, Hsu MF. J Polym Sci Part A Polym Chem 2002;40:524–34;
(b) Banerjee S, Madhra MK, Salunke AK, Jaiswal DK. Polymer 2003;44:613–22;
(c) Hsiao SH, Yang CP, Huang SC. Eur Polym J 2004;40:1063–74;
(d) Li F, Sang S, Ge JJ, Honigfort PS, Chen JC, Harris FW, et al. Polymer 1999;40(16):4571–83.

[17] Ghosh MK, Mittal KL, editors. Polyimides: fundamentals and applications. New York: Marcel Dekker; 1996. p. 71–120.

[18] Jeong KU, Kim JJ, Yoon TH. Polymer 2001;42:6019–30.

[19] (a) Ghassemi H, McGrath JE. Polymer 1997;38:3139–43;
(b) Lee CW, Kwak SM, Yoon TH. Polymer 2006;47:4140–7.

[20] Shobha HK, Johnson H, Sankarapandian M, Kim YS, Rangarajan P, Baird DG, et al. J Polym Sci Part A Polym Chem 2001;39:2904–10.

[21] (a) Fitch JW, Reddy VS, Youngman PW, Wohlfahrt GA, Cassidy PE. Polymer 2000;41:2301–4;
(b) Zhang YH, Tebby JC, Wheeler JW. Eur Polym J 1999;35:209–14.

[22] Chane-Ching K, Lequan M, Lequan RM, Kajzar F. Chem Phys Lett 1995;242:598–603.

[23] (a) Smith Jr JG, Connell JW, Hergenrother PM. Polymer 1994;35: 2834–9;
(b) Connell JW, Smith Jr JG, Hergenrother PM. Polymer 1995;36:5–11;
(c) Connell JW, Smith Jr JG, Hedrick JL. Polymer 1995;36:13–9;
(d) Smith Jr JG, Thompson CM, Watson KA, Connell JW. High Perform Polym 2002;14:225–39;
(e) Watson KA, Palmieri FL, Connell JW. Macromolecules 2002;35: 4968–74.

[24] Smith Jr JG, Connell JW, Hergenrother PM. Polym Prepr 1992;33: 241–7.

[25] Whitaker CM, Kott KL, McMahon RJ. J Org Chem 1995;60:3499–508.

[26] Miyatake K, Hay AS. J Polym Sci Part A Polym Chem 2001;39: 1854–9.

[27] (a) Yang CP, Su YY. Polymer 2003;44:6311–22;
(b) Hsiao SH, Yang CP, Chung CL. J Polym Sci Part A Polym Chem 2003;41:2001–18;
(c) Yang CP, Su YY, Hsiao FZ. Polymer 2004;45:7529–38;
(d) Yang CP, Su YY. Polymer 2005;46:5778–88;
(e) Chung CL, Yang CP, Hsiao SH. J Polym Sci Part A Polym Chem 2006;44:3092–102;
(f) Chen YY, Yang CP, Hsiao SH. Macromol Chem Phys 2006;207: 1888–98;
(g) Wang K, Yang SY, Fan L, Zhan MSH, Liu JG. J Polym Sci Part A Polym Chem 2006;44:1997–2006.

[28] Wang S, Ji Q, Tchatchoua CN, Shultz AR, McGrath JE. J Polym Sci Part B Polym Phys 1999;37:1849–62.

[29] Rata S, Ayambem A, McGrath JE, Wilkes GL. Polymer 2001;42(14): 6173–86.