

Light-Color Soluble Polyimides Based on α,α' -Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene and Aromatic Dianhydrides

Chin-Ping YANG,^{1,†} Ya-Ping CHEN,² Ea-Mor WOO,² and Shu-Hsien LI²

¹Department of Chemical Engineering, Tatung University, 40 Chungshan North Rd., 3rd Sec., Taipei, 104, Taiwan

²Department of Chemical Engineering, National Cheng Kung University, Tainan, 701, Taiwan

(Received December 8, 2005; Accepted January 9, 2006; Published May 15, 2006)

ABSTRACT: A fluorine-containing crystalline diamine, α,α' -bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene (**II**), was prepared through nucleophilic substitution reaction of 2-chloro-5-nitrobenzotrifluoride and α,α' -bis(4-hydroxyphenyl)-1,3-diisopropyl in the presence of potassium carbonate, followed by catalytic reduction with hydrazine and Pd/C. A series of polyimides (PIs) **V_{a-f}** were then synthesized from this diamine (**II**) by polymerizing with various commercially available aromatic dianhydrides (pyromellitic dianhydride (PMDA, **III_a**), 3,3',4,4'-benzopheno tetracarboxylic dianhydride (BTDA, **III_b**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, **III_c**), diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA, **III_d**), 4,4'-oxydiphthalic anhydride (ODPA, **III_e**) and 4,4'-hexafluoro isopropylidenediphthalic anhydride (6FDA, **III_f**)) via thermal (H) or chemical (C) imidization methods. The polyimides had inherent viscosities ranging from 0.60 to 0.95 dL/g. Except for the thermal imidization of **V_b**(H), the **V**-series polyimides were readily soluble in amide-type solvents, such as *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO), and also soluble even in less polar solvents such as *m*-cresol or pyridine. Most polyimides (film samples) had good tensile strengths of 70 to 110 MPa, elongations at break of 8 to 13% (except for **V_e**, 37%), and initial moduli of 1.7 to 2.0 GPa. The glass-transition temperatures of **V**-series polyimides were in 182–202 °C, and had good thermal stability of 10% weight loss temperatures (491–541 °C in nitrogen or 495–537 °C in air), and char yields at 800 °C in nitrogen ranging 46–61 wt %. Except for **V_{a,b}** series, the **V**(H) series had cutoff wavelengths between 364.5 to 399.5 nm and the *b** (yellowness index) values ranging from 12.7 to 39.5. The polyimides were found to possess low moisture absorption in the range of 0.19–0.91 wt %. [doi:10.1295/polymj.38.457]

KEY WORDS Fluorinated / Polyimide / α,α' -Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene /

Aromatic polyimides are well known as polymer materials of high performance for their excellent thermal stabilities, chemical resistance and electric properties.^{1–7} Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. Optical transparency of polyimide films is of special importance in some application such as flexible solar radiation protectors,⁸ orientation films in liquid crystal display devices,⁹ optical waveguides for communication interconnects,¹⁰ and optical half-wave plates for planar light-wave circuits.¹¹ However, most wholly aromatic polyimides strongly absorb in the visible region of their UV–vis spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer complex (CTC) formation. Besides, they are difficult to process because of high softening temperatures and limited solubility in commercially available solvents.

Consequently, continuing search of new polyimides with better process ability balanced with good thermal stability should be desirable for many applications.

From the molecular design principle, it is known that incorporation of ether groups or isopropyl groups into the main polyimide chains generally lead to lower glass transition temperatures (T_g), as well as significant improvement of the solubility and the thermo-plasticity of the polymers. Additionally, introduction of bulky groups into the polymer main chain or attachment of bulky pendant groups can impart significant increase in T_g by restricting the segmental mobility, while providing a good solubility due to decreased order of packing and lower crystallization. In responding to increasing optical applications of polyimides, a number of very lightly colored to completely colorless transparent polyimide films have been synthesized and characterized. A pervious work¹² has shown the formation of CTC between an alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. Lowering the CTC generally affords polyimides with lighter color.

Recently, low-dielectric-constant polymers have found diverse applications in the electronics industry as flexible circuitry substrates, stress buffers, interlayer

[†]To whom correspondence should be addressed (E-mail: emwoo@mail.ncku.edu.tw).

dielectrics, and passivation layers. Development of low-dielectric-constant and thermally stable polymers has been quite dramatic and has drawn the attention of many polymer scientists. Aromatic polyimides possess many useful properties and are increasingly being required by the electronic circuit industry.^{5,13} A low dielectric constant is one of the most attractive properties of polyimide materials for electronic applications. One of the most effective methods to decrease the dielectric constant is to introduce fluorine atoms into polyimides.¹³ Fluorination is also known to enhance the solubility and optical transparency and to lower moisture absorption of polyimides.^{14–16} Therefore, it is expected that fluorinated polyimides will be widely applied in electro-optical or semiconductor industries. Recent studies have demonstrated that polyimides derived from ether-bridged aromatic diamines with a trifluoromethyl (3F) group are generally soluble with low moisture uptakes, low dielectric constants, high optical transparency, and low birefringence.^{17–21}

A previous study²² has demonstrated that the PIs based on an amine, α,α' -bis[4-(4-aminophenoxy)phenyl]-1,3-diisopropylbenzene (**II'**), show excellent processability and mechanical properties. In patents, other investigators have also reported similar amine monomers with fluorines, trifluoromethyl diamines, which could be used to synthesize PI's exhibiting thermotropic liquid crystalline properties.^{23,24} In earlier works of this laboratory, we have also demonstrated property improvements in a series of soluble fluorinated polyamides and poly(amide-imide)s synthesized from a fluorinated diamine [1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene], with various aromatic diacids or imide-containing diacids.^{25,26} In this study, a fluorinated crystalline diamine monomer, α,α' -bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene (**II**), was first prepared by the reaction of 2-chloro-5-nitrobenzotrifluoride and α,α' -bis(4-hydroxyphenyl)-1,3-diisopropyl. This fluorinated amine monomer was subsequently polycondensed with various commercially available aromatic dianhydrides **III_{a–f}** to produce a series of fluorinated polyimides (**V_{a–f}**). The fluorinated polyimides were further subjected to various characterizations on solubility, moisture absorption, thermal, optical properties. The characteristic properties of these polyimides were then compared to the properties of non-fluorinated counterpart of polyimides (code-name: **VI**), which were used as basis of property comparisons.

EXPERIMENTAL

Materials

The following chemicals: 2-chloro-5-nitrobenzotrifluoride (Acros), α,α' -bis(4-hydroxyphenyl)-1,3-

diisopropylbenzene (Mitsui Petrochemicals Ind. (Japan), 10% palladium (Fluka), acetic anhydride (from Fluka), and hydrazine monohydrate (TCI), were used as received. Aromatic dianhydrides: pyromellitic dianhydride (PMDA, **III_a**) (TCI), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA, **III_b**) (TCI), 4,4'-oxydiphthalic anhydride (ODPA, **III_c**) (TCI), and diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA, **III_d**) (New Japan Chemicals Co.) were re-crystallized from acetic anhydride before use. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA, **III_e**) (Chriskev) and 4,4'-hexafluoro isopropylidene-diphthalic anhydride (6FDA, **III_f**) (Hoechst) were purified by sublimation. *N*-Methyl-2-pyrrolidone (NMP, Fluka), *N,N*-dimethyl acetamide (DMAc, Fluka), *N,N*-dimethyl formamide (DMF, Fluka), and pyridine (Py, Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Measurements

IR spectra were recorded on a Fourier-Transform Infrared Spectrometer FT-IR-720 (Horiba Corp., Japan). Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer. ¹H and ¹³C spectra were recorded on a JEOL EX-500 FT-NMR spectrometer. Although the NMR apparatus is capable of as high as 500 MHz, actual characterizations were usually performed at lower frequencies, as specified in the data.

Inherent viscosities were determined at 0.5 g/dL concentration using an Ubbelohde viscometer at 30 °C. X-Ray crystallographic data were collected on a Nonius Kappa CCD XRD diffractometer. The molecular structure was solved on a VAX-3300 computer using NRCC SDP software. Thermogravimetry analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on 9–11 mg film samples heated in flowing nitrogen or air (100 cm³/min) at a heating rate of 20 °C/min. Differential scanning calorimeter (DSC) traces were measured on TA Instruments DSC 2010 at the rate of 15 °C/min in flowing nitrogen (40 cm³/min). Glass transition temperatures were read as the midpoint of the heat capacity jump and were taken from the second heating scan after a quick quenching down from 400 °C.

Mechanical properties of the films were measured using a tensile tester (Instron model 1130) with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 40–50 μm thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used.

The color intensity of the polymers was evaluated by a Macbeth Color-eye colorimeter. Measurements were performed with films, using an observational

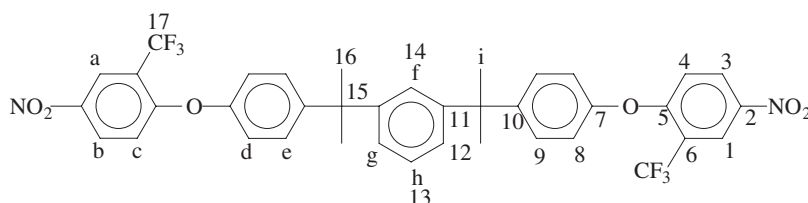
angle of 10° and a CIE (Commission International de l'Éclairage)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer.

The equilibrium moisture absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 d. Weight-average molecular weights (M_w 's) and number-average molecular weights (M_n 's) were obtained *via* gel permeation chromatography (GPC, Waters 2410) on the basis of a standard of polystyrene calibration and tetrahydrofuran (THF) as the eluent.

Monomer Synthesis

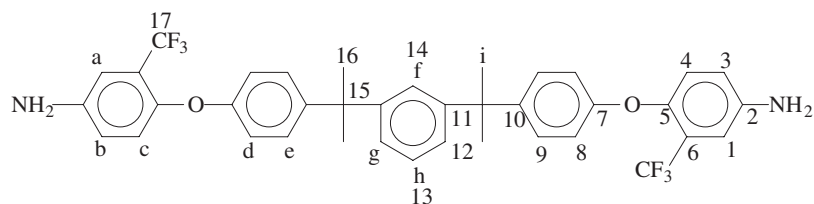
Synthesis of α,α' -Bis[4-(4-nitro-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene (I). α,α' -Bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (8.66 g, or 25 mmol) and 2-chloro-5-nitrobenzotrifluoride (11.50 g, or 51 mmol) were first dissolved in 18 mL of DMF in a 100-mL flask with stirring. After the mixture was completely dissolved, potassium carbonate (5 g, or 36 mmol) was added to it in one portion, and the mixture was heated at 110 °C for 12 h. The mixture was allowed to cool and then poured into 70 mL of methanol to give a solid, which was collected, washed thoroughly with methanol, warm water,

and dried. The crude product was re-crystallized from DMF/methanol to gain fine crystals weighed 17 g (yield 94%, DSC mp = 129 °C) (Literature value. m.p. = 127–128 °C).²⁴ IR (KBr): 1533, 1336 (–NO₂ stretching), 1288, 1270, 1197, 1159, 1147 cm⁻¹ (C–F and C–O stretch). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.43–8.43 (s, 2H, H_a), 8.41–8.39 (d, 2H, H_b), 7.28–7.27 ppm (d, 4H, H_c), 7.23–7.18 (t, 1H, H_h), 7.10–7.09 (d, 2H, H_g), 7.07–7.05 (d, 4H, H_d), 7.03 (s, 1H, H_f), 6.99–6.97 (d, 2H, H_c), 1.61 (s, 12H, H_i). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 160.25 (C⁵), 151.45, (C⁷), 149.49 (C¹¹), 148.27 (C²), 141.51 (C¹⁰), 130.01 (C¹³), 128.78 (C⁹), 127.92 (C¹⁴), 125.29 (C³), 123.78 (C¹²), 123.34 (C¹, quartet, ³J_{C–F} = 5 Hz), 125.52, 123.34, 121.17, 119.21 (C¹⁷, quartet, with ¹J_{CF} = 271 Hz), 119.76 (C⁸), 119.21, 118.96, 118.70, 118.44 (C⁶, quartet, with ²J_{CF} = 31 Hz), 117.73 (C⁴), 42.45 (C¹⁵), 30.44 (C¹⁶). ¹H NMR data are usually influenced by neighboring protons and splitting into multiplex peaks with overlapping, which was a problem. J values for these peaks were not analyzed; instead, for ¹³C NMR spectroscopic data, there is only one peak, which can be split only by neighboring F atom. Therefore, ¹³C NMR data were used for such purpose. Elemental analysis: calculated for (I) C₃₈H₃₀F₆N₂O₆ (724.66): C, 62.98%; H, 4.17%; N, 3.82%. Found: C, 62.83%; H, 3.97%; N, 3.67%.



α,α' -Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene (II). To a suspension solution of the purified dinitro compound I (7.24 g, 10 mmol) and 10% Pd/C (0.1 g) in ethanol (70 mL), hydrazine monohydrate (2.2 mL) was added drop wise to the stirred mixture at 70–80 °C within 30 min. After complete addition, the mixture was heated at the reflux temperature for about 2 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was first concentrated to 1/3 volume, then cooled to precipitate white-color crystals. They were dried in vacuum at room temperature to gain II 6.49 g (yield 97.7%, DSC mp = 125 °C) (Literature value²⁴ m.p. = 118–119 °C). IR (KBr): 3300–3500 (N–H stretching), 1267, 1228, 1160, 1137 cm⁻¹ (C–O and C–F stretch). ¹H NMR (500 MHz, CDCl₃): δ = 7.23–7.20 (t, 1H, H_h), 7.16 (s, 1H, H_f), 7.16–7.15 (d, 4H, H_c), 7.11–

7.09 ppm (d, 2H, H_g), 6.97–6.97 (s, 2H, H_a), 6.87–6.86 (d, 6H, H_{b,d}), 6.78–6.76 (d, 2H, H_c), 1.67–1.65 (s, 12H, H_i). ¹³C NMR (125 MHz, CDCl₃): δ = 155.82 (C⁷), 150.05, (C¹¹), 146.43 (C⁵), 145.3 (C²), 142.17 (C¹⁰), 127.86 (C⁹), 127.50 (C¹³), 125.30 (C¹⁴), 124.03 (C¹²), 126.46, 124.33, 122.20, 120.07 (C¹⁷, quartet, with ¹J_{CF} = 271 Hz), 122.17 (C⁴), 122.99, 122.73, 122.48, 122.20 (C⁶, quartet, with ²J_{CF} = 31 Hz), 119.31 (C³), 117.09 (C⁸), 112.90 (C¹, quartet, ³J_{C–F} = 5 Hz), 42.49 (C¹⁵), 30.77 (C¹⁶). Note that ¹H NMR has a range of 1–10 ppm. The amino group is outside this range and cannot be described. The amino group could be measured using IR, instead of NMR. Elemental analysis calculated for (II) C₃₈H₃₄F₆N₂O₂ (664.67): C, 68.67%; H, 5.16%; N, 4.21%. Found: C, 68.89%; H, 4.95%; N, 4.01%.



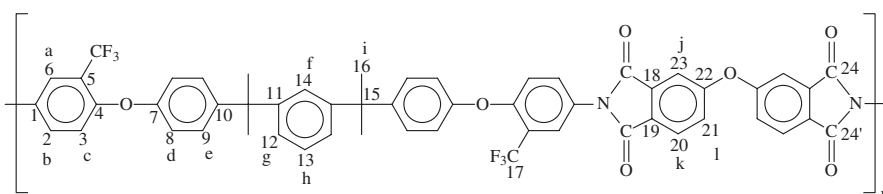
X-Ray Structure Analysis. The single crystals of diamine compound **II** were grown during slow crystallization of ethanol solution. A crystal size of $0.3 \times 0.20 \times 0.15$ mm was used for X-ray structure determination. Intensity data were collected on a Nonius Kappa CCD XRD diffractometer at 295 K with graphite-monochromatized Mo K_{α} radiation ($\lambda = 0.71073$ Å). Compound **II** crystallized in a triclinic system with space group P1 [$M_w = 664.47$, $a = 11.3250(2)$ Å, $b = 12.7130(2)$ Å, $c = 12.9320(2)$ Å; $\alpha = 111.8030(10)^{\circ}$, $\beta = 100.1160(10)^{\circ}$, $\gamma = 97.9110^{\circ}$ where $D_c = 1.33$ g/cm³ for $Z = 2$ and $V = 1659.37(5)$ Å³]. Least-squares refinement based on 7515 independent reflections converged to final $R_1 = 0.0582$ and $wR_2 = 0.1495$. The crystal structure was solved on a VAX-3300 computer using NRCC SDP (SDP = Structure Determination Package) software. The molecular structure for 3F-diamine compound **II** is shown in Figure 4.

Synthesis of Polyimides

Thermal Cyclodehydration. Diamine **II** (0.465 g, 7 mmol) was dissolved in 4.8 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.1526 g (7 mmol) PMDA **III_a** was added to it in one portion. The mixture was stirred at room temperature for 8 h to form a poly(amic acid) solution. The poly(amic acid) solution then was poured into a glass dish (diameter $\phi = 9$ cm), which was placed in an 80 °C oven for 1 h to remove the solvent. The semi-dried poly(amic acid) film was further dried and imidized by sequential heating at 130 °C for 20 min, 150 °C for 20 min, 180 °C for 20 min, 210 °C for 20 min, and 250 °C for 30 min. By soaking in

water, a flexible polyimide film **V_a** could be easily stripped off from the glass surface. The inherent viscosity of **V_a(H)** in DMAc at a 0.5 g/dL concentration at 30 °C was 0.69 dL/g.

Chemical Cyclodehydration. In a method similar to that of synthesizing the poly(amic acid) solution, a 0.6-mL mixture of acetic anhydride and Py (volume ratio 2:1) then was added to the poly(amic acid) solution. The poly(amic acid) solution was imidized by stirred in oil bath at 80–100 °C for 1 h, and obtained solution was poured into a glass culture dish ($\phi = 9$ cm), which was placed in a 110 °C oven for 1 h to remove the solvent. The semi-dried polyimide film was further processed as a manner in above. The inherent viscosity of **V_b(C)** in DMAc at a 0.5 g/dL concentration at 30 °C was 0.6 dL/g. In the IR spectra of polyimide **V_a** obtained by thermal treatment, characteristic imide group absorption peaks around 1781, 1731 (imide C=O), 1380 (C–N stretch), 1093, 725 cm⁻¹ (imide ring deformation). ¹H NMR for **V_e** (500 MHz, CDCl₃, δ , ppm): 8.04–8.02 (d, 2H, H_k), 7.77 (s, 2H, H_a), 7.58 (s, 2H, H_j), 7.52–7.51 (d, 4H, H_{b,1}), 7.28–7.26 (d, 4H, H_e), 7.26–7.23 (t, 1H, H_h), 7.20 (s, 1H, H_f), 7.19–7.10 (d, 2H, H_g), 7.04–7.02 (d, 6H, H_{d,c}), 1.70 (s, 12H, H_i). ¹³C NMR for **V_e** (125 MHz, CDCl₃, δ , ppm): 165.89, 165.79 (C^{24,24'}), 151.17 (C²²), 155.54 (C⁷), 153.13 (C⁴), 149.84 (C¹¹), 147.47 (C¹⁰), 134.34 (C¹⁸), 131.08 (C¹), 128.38 (C⁹), 127.67 (C¹³), 127.03 (C¹⁴), 126.34 (C²⁰), 125.43 (C¹²), 125.14 (C¹⁹), 124.94 (C²), 124.19 (C³, C²¹), 126.02, 123.85, 121.68, 119.44 (C¹⁷, quartet, ¹J_{C-F} = 271 Hz), 121.54, 121.28, 121.02, 120.76 (C⁵, quartet, ²J_{C-F} = 33 Hz), 119.44 (C⁸), 118.57 (C⁶), 114.00 (C²³), 42.72 (C¹⁵), 30.80 (C¹⁶).



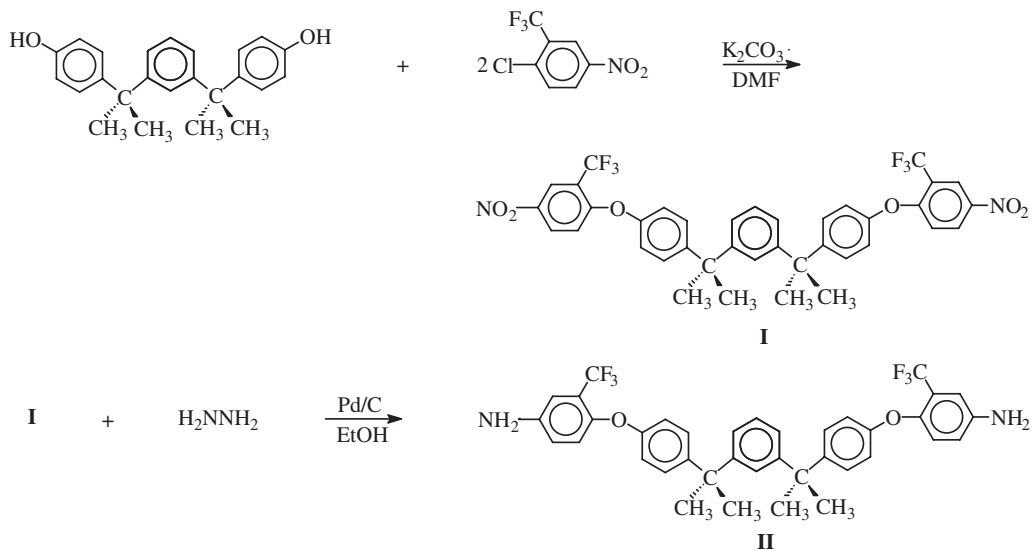
RESULTS AND DISCUSSION

Monomer Synthesis

The fluorinated diamine, α, α' -bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene (**II**), was prepared through the nucleophilic substitu-

tion reaction of 2-chloro-5-nitrobenzotrifluoride with α, α' -bis(4-hydroxy phenyl)-1,3-diisopropylbenzene in the presence of potassium carbonate, followed by catalytic reduction with hydrazine and Pd/C (Scheme 1).

Owing to the fact that the reaction activity of 2-chloro-5-nitrobenzotrifluoride with bisphenol is higher than that of 1-chloro-4-nitrobenzene, both the reac-



Scheme 1. Synthesis of 3F-diamine **II**.

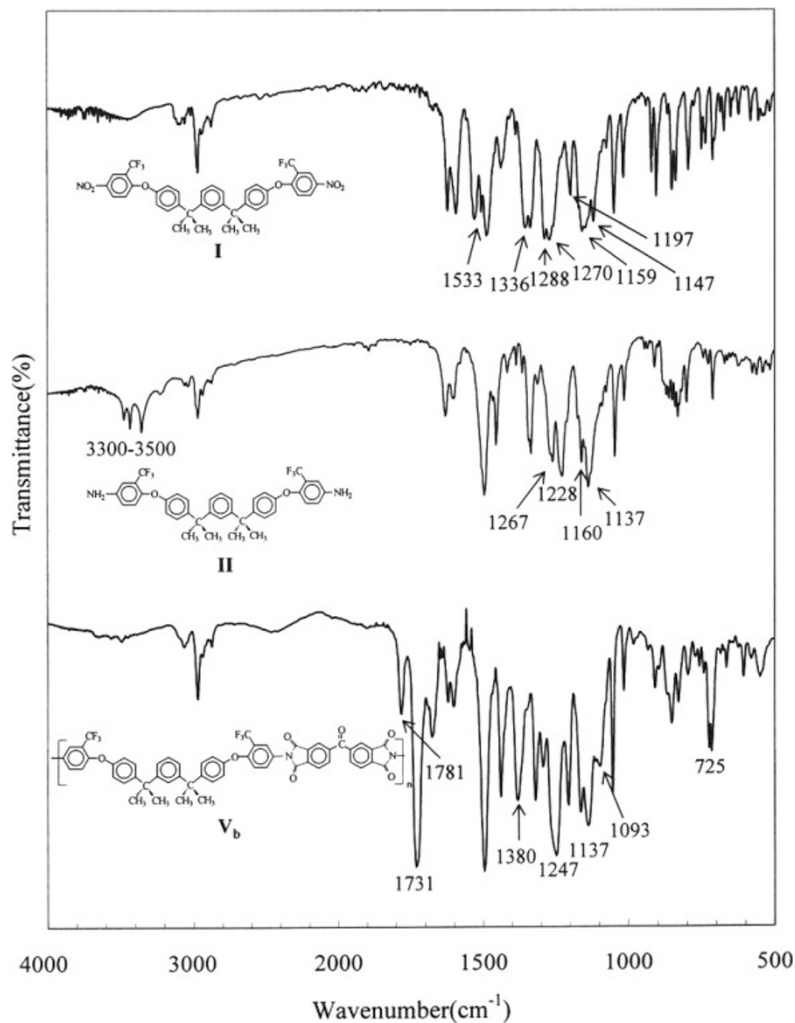


Figure 1. FT-IR spectra for 3F-dinitro compound **I**, 3F-diamine **II**, and PI **V_b**.

tion temperature and the amount of K_2CO_3 could be reduced to avoid producing the coloring dinitro-compounds. In this study, reaction proceeded at 100°C for

8 h could yield better results.

FT-IR, NMR, elemental analysis, and X-ray were used to confirm the structures of the intermediate **I**

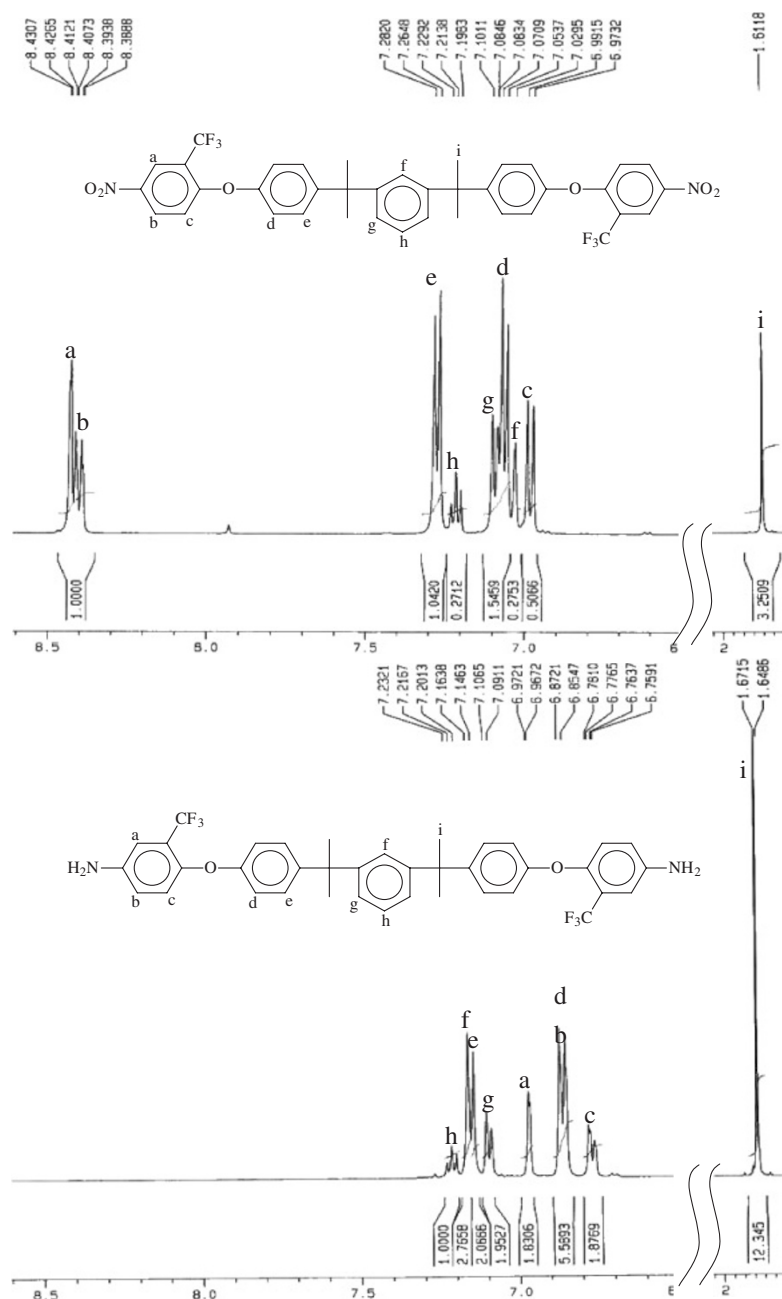


Figure 2. ^1H spectra for dinitro compound **I** and diamine **II** in $\text{DMSO-}d_6$ and CDCl_3 .

and the diamine monomer **II**. They are discussed in sequence here. Figure 1 shows the FT-IR spectra of dinitro compound **I** and diamine **II**. The nitro group of compound **I** displays two characteristic bands at 1533 and 1336 cm^{-1} (NO_2 asymmetric and symmetric stretching). After reduction, the figure shows that the characteristic absorptions of the nitro group disappears, and the amino group shows a pair of N–H stretching bands in the region of $3300\text{--}3500\text{ cm}^{-1}$.

Figures 2 and 3 present the ^1H and ^{13}C NMR spectra for dinitro compound **I** and diamine **II**, respectively. The absorption signals of aromatic protons of **I** appear in the region of $6.973\text{--}8.431$ ppm, and those of **II** shifted to higher field between $6.759\text{--}7.232$ ppm. In

the ^1H NMR spectrum of **I**, the protons H_a (8.431 ppm) and H_b (8.427 ppm) resonate at the farthest downfield region due to the inductive effect of electron withdrawing $-\text{NO}_2$ and $-\text{CF}_3$ groups; the protons H_d (7.062 ppm) and H_c (6.982 ppm) ortho-oriented to aromatic ether appear in an upfield region due to the electron-donating property of aromatic ether. After reduction, the protons H_a (6.969 ppm) and H_b (6.864 ppm) of **II** shift to an upfield region due to the electron-donating property of amino groups. In ^{13}C NMR spectra, all the carbon-13 atoms in **I** and **II** show 17 signals, which resonate in the region of $30.44\text{--}160.25$ and $30.77\text{--}155.82$ ppm, respectively. The ^{13}C NMR spectrum of **I** shows three quartets because of hetero-

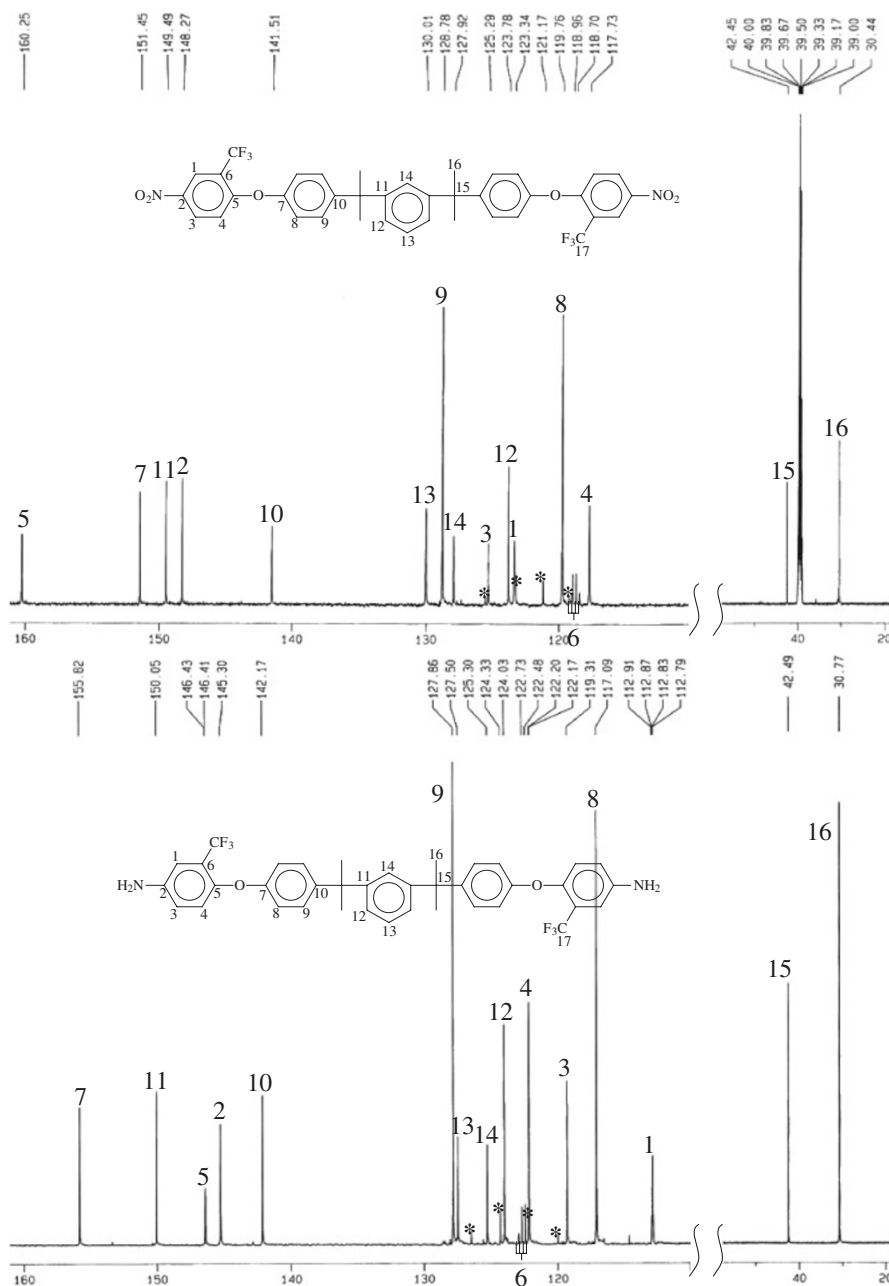


Figure 3. ^{13}C spectra for dinitro compound **I** and diamine **II** in $\text{DMSO-}d_6$ and CDCl_3 .

nuclear ^{13}C – ^{19}F coupling. The large quartet centered at about 122 ppm is due to the CF_3 carbon. The one-bond C–F coupling constant in this case is about 271 Hz. The CF_3 -attached carbon (C^6) also shows a clear quartet centered at about 119 ppm with a smaller coupling constant of about 31 Hz due to two-bond C–F coupling. In addition, the C^1 carbon (ortho to CF_3 group) also has resonance split by the three fluorines (three-bond coupling). The close quartet has an even smaller coupling constant (*ca.* 5 Hz) because the interaction operates over more bonds. Similar splitting patterns ($^1J_{\text{C-F}} = 271$ Hz, $^2J_{\text{C-F}} = 31$ Hz, and $^3J_{\text{C-F}} = 5$ Hz) are also found in the ^{13}C NMR spectrum of **II**. All the spectroscopic data are in good agreement with the expected structures.

In addition, Figure 4 illustrates the crystal structure of diamine **II**. The five phenylene rings of **II** cannot be all in the same plane because of steric hindrance by the CF_3 group and isopropylidene group. This hindrance disturbs the co-planarity of the aromatic unit, leading to enhancement of solubility of the polyimides.

Polymer Synthesis

All the polymers **V**_{a-f} were synthesized from diamine **II** and dianhydrides **III**_{a-f}, by a conventional two-step procedure ring-opening polyaddition at room temperature to poly(amic acid)s **IV**, followed by sequential heating to 250 °C or treatment with a mixture of $\text{Ac}_2\text{O/Py}$ to obtain the corresponding polyimides,

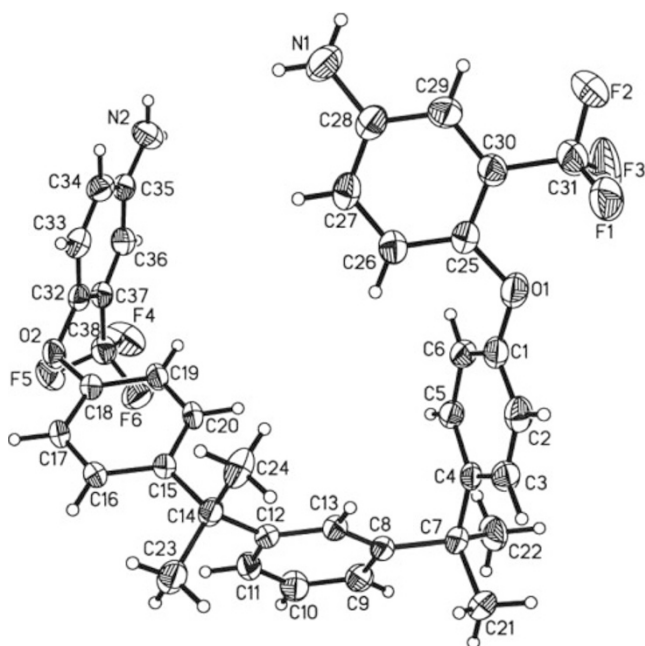
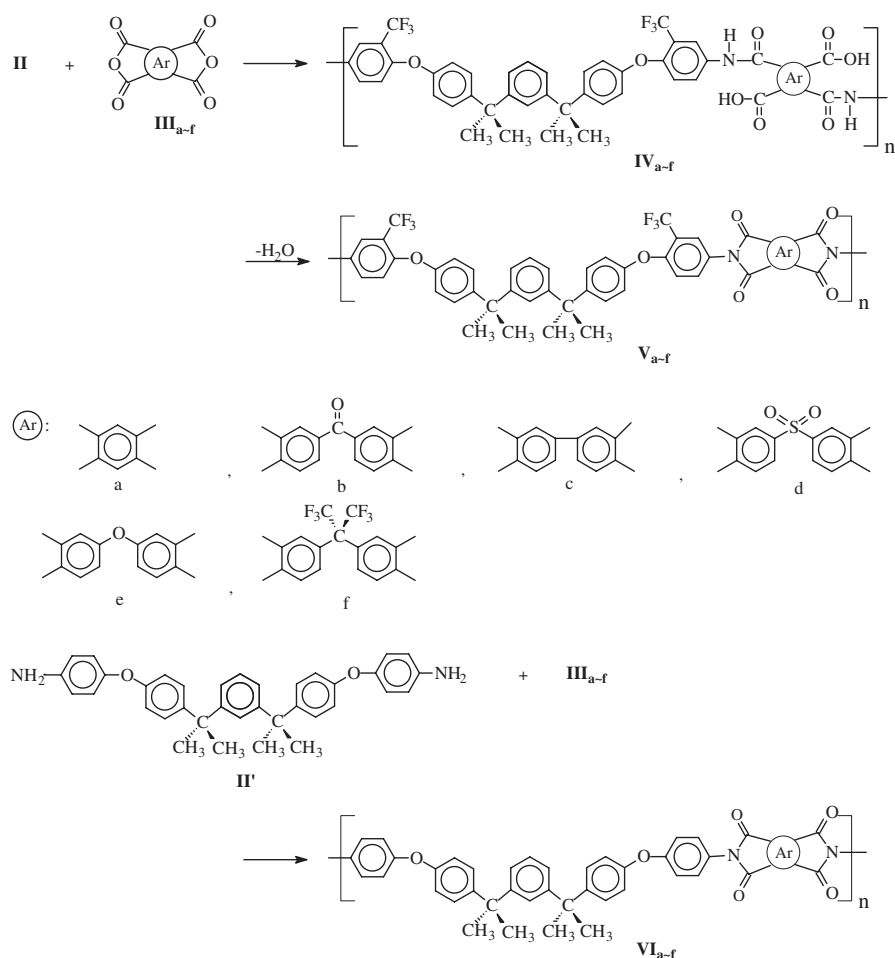


Figure 4. X-Ray single crystallography for the diamine compound **II**.

as shown in Scheme 2.

Transformation from poly(amic acid) to polyimides was possible *via* thermal or chemical cyclodehydrations. Merits of the former are easy to handle and to cast into thin films, and those of the latter were easy to prepare soluble polyimides. Figure 5 presents the variation curves of inherent viscosities of the poly(amic acid)s obtained from 6FDA with CF₃-containing diamine **II** or non-fluorinated **II'** at various times. The reaction of 6FDA with fluorinated **II** proceeded relatively slow and its inherent viscosity reached 0.78 dL/g after 4 h. After this point, inherent viscosity increased slowly and reached 0.81 dL/g in 5 h; polymerization nearly ceased and no increase in the inherent viscosity was observed after 8 h. The reaction of 6FDA with non-fluorinated **II'** proceeded relatively fast and its inherent viscosity increased fast within 30 min; inherent viscosity reached 1.00 dL/g after 60 min and not increased anymore. GPC curve for the PIs showed that the M_w and M_n values cover a range from 6.98×10^4 – 12.51×10^4 and 5.09×10^4 – 9.13×10^4 g/mol, respectively, and the polydispersity index (M_w/M_n) value is 1.2–1.6 (polystyrene standard) (Table I).



Scheme 2. Synthesis of polyimides.

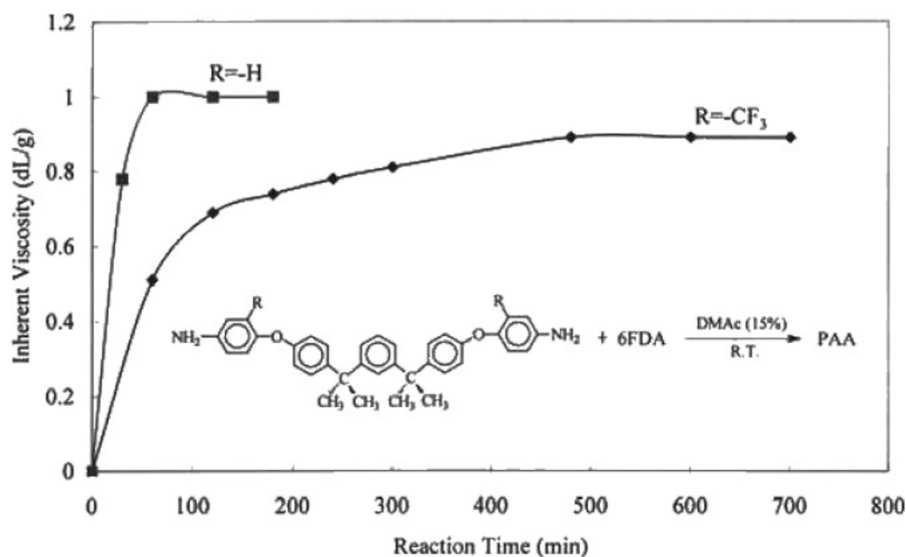


Figure 5. Viscosity change in poly(amic acid)s prepared in DMAc with 15% solid contents at room temperature.

Table I. Inherent viscosity and molecular weights of organo-soluble fluorinated polyimides

Polyimide ^a	η_{inh}^b (dL/g)	GPC Data for Polyimides ^c		
		$M_w^b \times 10^4$	$M_n^b \times 10^4$	M_w/M_n
V _a	0.69	8.06	5.09	1.6
V _b (C)	0.60	— ^d	— ^d	—
V _c	0.79	8.01	5.41	1.5
V _d	0.95	10.78	7.82	1.4
V _e	0.66	6.98	5.95	1.2
V _f	0.90	12.51	9.13	1.4

^aPolyimides obtained by the thermal imidization method.

^bMeasured at a concentration of 0.5 g/dL in DMAc at 30 °C.

^cMeasured by GPC in THF, relative to polystyrene standards.

^dThe polyimide is insoluble in THF.

The formation of polyimides was confirmed by means of elemental analysis, IR and NMR spectroscopy. The typical IR spectrum of V_b is shown earlier in Figure 1. All polyimides exhibited characteristic imide group absorptions around 1781 and 1731 cm⁻¹ (typical of imide carbonyl asymmetrical and symmetrical stretch), 1380 cm⁻¹ (C–N stretch), and 1093 and 725 cm⁻¹ (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm⁻¹ due to the C–O and C–F stretching. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the poly(amic acid) precursor into polyimide.

Figure 6 shows the ¹H and ¹³C NMR spectra of soluble polyimide V_e. In ¹H NMR spectrum, all the protons resonated in the region of 7.018–8.035 ppm. The H_k (8.027 ppm), H_a (7.772 ppm), H_j (7.584 ppm), H_{b,l} (7.514 ppm) close to the imide ring appears at the farthest downfield region of the spectrum, owing to the resonance. The H_{c,d} (7.027 ppm) is shifted to a

Table II. Elemental analysis of polyimides

Polymer ^a	Formula (Molecular weight)	Elemental Analysis (%) ^a			
		C	H	N	
V _a	(C ₄₈ H ₃₂ O ₆ N ₂ F ₆) _n	Calc	68.08	3.81	3.31
	(846.78) _n	Found	67.29	3.53	3.28
V _b	(C ₅₅ H ₃₆ O ₇ N ₂ F ₆) _n	Calc	69.47	3.82	2.95
	(950.89) _n	Found	69.82	3.83	2.24
V _c	(C ₅₄ H ₃₆ O ₆ N ₂ F ₆) _n	Calc	70.28	3.93	3.04
	(922.88) _n	Found	70.10	3.73	2.74
V _d	(C ₅₄ H ₃₆ O ₈ N ₂ F ₆ S ₁) _n	Calc	65.72	3.68	2.84
	(986.94) _n	Found	65.90	3.62	2.73
V _e	(C ₅₄ H ₃₆ O ₇ N ₂ F ₆) _n	Calc	69.08	3.86	2.98
	(938.88) _n	Found	68.88	3.65	2.65
V _f	(C ₅₇ H ₃₆ O ₆ N ₂ F ₁₂) _n	Calc	63.81	3.38	2.61
	(1072.90) _n	Found	63.84	3.39	2.33

^aPolyimides obtained by the thermal imidization method.

higher field due to the electron donating property of aromatic ether. In ¹³C NMR spectra, all the carbon-13 atoms in V_e show 24 main signals, and carbon C^{24,24'} of the carbonyl group is evidenced in the downfield region. The quartet centered at about 123 ppm is due to the CF₃ carbon (C¹⁷). The one-bond C–F coupling constant in this case is about 271 Hz. The CF₃-attached carbon (C⁵) also shows a clear quartet centered at about 121 ppm with a smaller coupling constant of about 33 Hz due to two-bond C–F coupling. The results of elemental analysis of V_{a–f} are listed in Table II. The above results show that polymer series V has been synthesized successfully.

Properties of Polymers

Solubility Test. Solubility of the polyimides was tested in various organic solvents, and the results are summarized in Table III. Polymers V_{a–f} had excellent

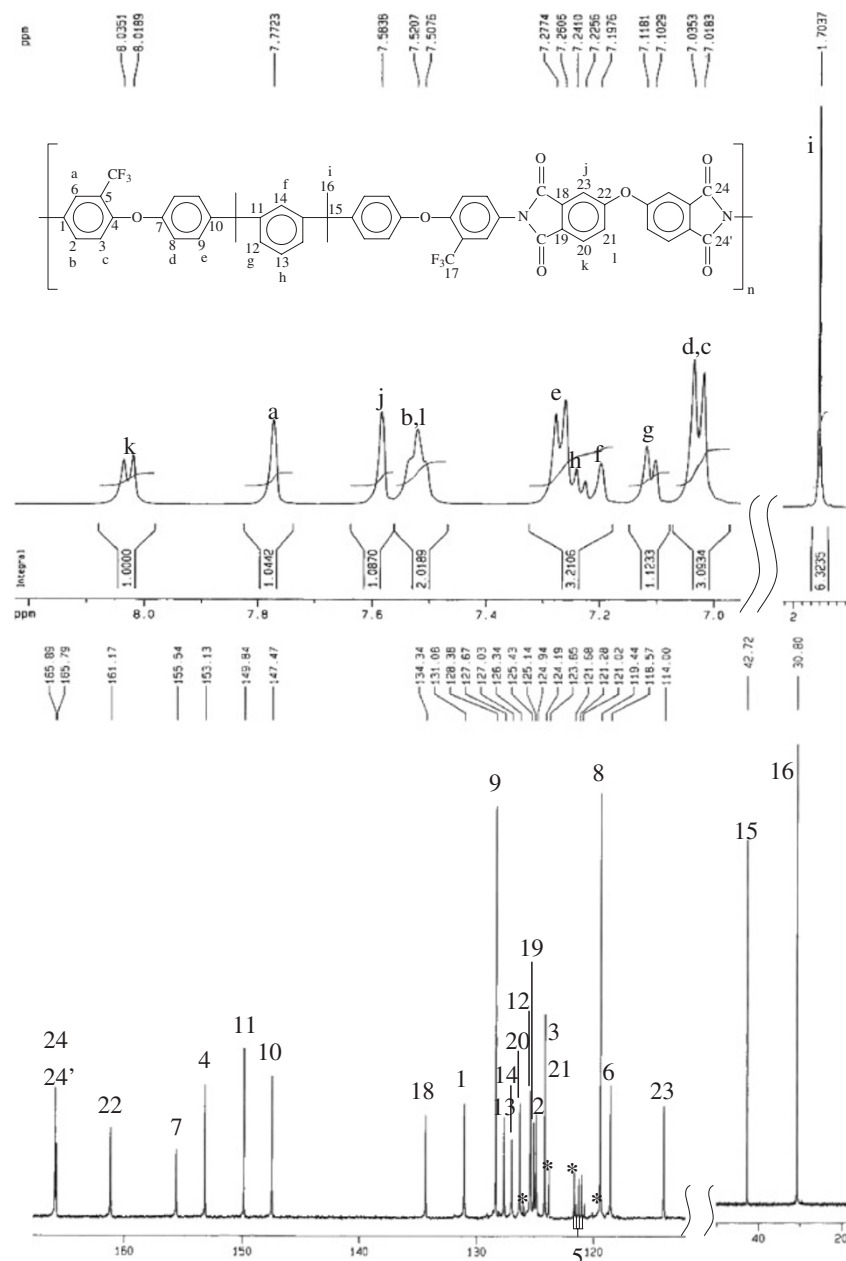


Figure 6. ^1H and ^{13}C NMR spectra for PI **V_e** in CDCl_3 .

solubility in aprotic polar solvents, such as NMP, DMAc, DMF, and DMSO, and they were also easily soluble in less polar solvents like *m*-cresol and pyridine at room temperature or after heating. Polyimide **V_b(H)** prepared *via* thermal imidization was insoluble in all tested solvents, including concentrated sulfuric acid. This may be attributed to the formation of some intermolecular links of the C=O group of BTDA during the thermal imidization.^{27–29} On the contrary, **V_b(C)** synthesized *via* chemical imidization did not possess crosslinks and exhibited better solubility. In addition, the solubilities for the analogous polyimides **VI_{a–f}** from an earlier study²² have been listed here for comparative purposes. By comparing with the non-fluorinated polyimides **VI_{a–f}**, the solubility of **V_{a–f}** is

better than **VI_{a–f}**. The large differences in solubility between the **V** and **VI** series are attributed to the bulky CF₃ group, which increases the disorder in the chains and hinders denser chain stacking, thereby reducing the inter-chain interactions to enhance the solubility.

Optical Properties. The color intensities of the polyimides **V_{a–f}** were elucidated from the yellowness or redness indices observed by a Macbeth color-eye colorimeter. For comparison, the corresponding polyimides **VI_{a–f}** without the CF₃ groups were also prepared and characterized by their color intensity. The color coordinates of these polyimides are given in Table IV. The results indicate that the **V** series polyimides show a lower *b** value (a yellowness index) in contrast with the corresponding polyimides (the

Table III. Solubility^b behavior of polyimides

Polymers ^a	Solvents ^c									
	NMP	DMAc	DMF	DMSO	Py	<i>m</i> -Cresol	Dioxane	THF	CH ₂ Cl ₂	CHCl ₃
V _a (H)	+++	+++	+++	++	+++	+–	+++	+++	+++	++
V _b (H)	–	–	–	–	–	–	–	–	–	–
V _c (H)	+++	+++	+++	–	+++	+–	+++	+++	+++	S
V _d (H)	+++	+++	+++	+++	+++	+–	+++	+++	+++	+++
V _e (H)	+++	+++	+++	+++	+++	+–	+++	+++	+++	+++
V _f (H)	+++	+++	+++	+++	+++	+–	+++	+++	+++	+++
V _a (C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
V _b (C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
V _c (C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
V _d (C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
V _e (C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
V _f (C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
VI _a (C) ^d	–	–	–	–	–	–	–	–	–	–
VI _b (C)	+	+	+	–	+	+	S	S	S	S
VI _c (C)	–	–	–	–	–	–	–	–	–	–
VI _d (C)	–	–	–	–	–	–	–	–	–	–
VI _e (C)	+	+	+	+	+	+	+	+	+	+
VI _f (C)	+	+	+	+	+	+	+	+	+	+

^a(H):Polyimides obtained by the thermal imidization method. (C): Polyimides obtained by the chemical imidization method with DMAc as the solvent. ^bSolubility marks: (+++) greater than 10% w/V, (++) greater than 5% w/V, (+) greater than 1% w/V, (+–) partially soluble on heating, (S)swelling (1%) on heating, (–) insoluble on heating. ^cNMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; Py, pyridine; THF, tetrahydrofuran. ^dRef 14.

VI series). Figure 7 shows that the color intensity of polyimides was affected by the dianhydride moieties with a decreasing order: PMDA > BTDA > DSDA > BPDA > ODPa > 6FDA. On comparing the polymers of thermal cyclodehydration with those of the chemical cyclodehydration, films V_{a–f}(C) show a lower *b** value than V_{a–f}(H), which can be attributed to the chemical cyclodehydration, which prevents the polyimides from being oxidized/colored upon imidization.

Moreover, the color intensities of the polyimides could also be elucidated from the cut-off wavelength (λ_0) observed in the UV–vis absorption spectra and the λ_0 from these spectra are also listed in Table IV. The cut-off wavelength is defined to be 0.3%. In agreement with the results obtained from the colorimeter, all V series polyimides containing the pendant CF₃ group revealed a shorter cutoff wavelength than their respective analogue series VI polyimides, and this gave the V series a lighter color. The light colors of the polyimides with the CF₃ groups in their diamine moieties could be explained from the decreased intermolecular interactions. The 6FDA and ODPa produced fairly transparent and almost colorless polyimide films in contrast to other dianhydrides. These results could be attributed to the reduction of the intermolecular CTC between the alternating electron-do-

nor (diamine) and electron-acceptor (dianhydride) moieties or a blue-shift of an intramolecular CT absorption band. Earlier, Hasegawa and Horie³⁰ have concluded that bulky and electron-withdrawing CF₃ group in diamine II is effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect. The electron-withdrawing effect of the CF₃ groups on the diamine also may result in a blue-shift of an intramolecular CT absorption band by decreasing the electron-donating property of diamine moieties.

Tensile Properties. All the fluorinated polyimides were readily made into good-quality films for mechanical testing. The tensile properties of flexible films are summarized in Table V. They show an ultimate tensile strength of 70–110 MPa, an elongation to break of 8–37%, and an initial modulus of 1.7–2.0 GPa. Polyimides of V_a and V_c show a distinct yield point in stress-strain curve (yield strength: 80 and 72 MPa, respectively). Polyimides V_c obtained from BPDA show the largest elongation to break among this series, indicating high toughness. The similar tensile properties of all V series and analogue series VI polyimides show that the introduction of the CF₃ group in the main chain will not affect the excellent tensile properties of aromatic polyimides.

Thermal Properties. Both DSC and TGA were

Table IV. Color coordinates and the cut-off wavelength (λ_o) from UV-vis spectra for both V and VI series polyimide films

Polymer Code ^a	Color Coordinates ^b			Cut-off Wavelength (nm)	Film Thickness (μm)
	b^*	a^*	L^*		
standard	0.98	-0.4	96.2		
V_a(H)	68.6	-8.1	88.7	416.0	55
V_b(H)	55.8	-8.4	89.3	404.5	43
V_c(H)	22.5	-8.4	55.8	394.0	36
V_d(H)	39.5	-7.7	90.3	399.5	76
V_e(H)	12.7	-2.8	94.1	364.5	38
V_f(H)	14.7	-3.7	91.2	370.0	52
V_a(C)	45.3	-17.6	91.6	389.0	40
V_b(C)	30.5	-10.5	94.6	399.0	75
V_c(C)	15.6	-6.3	92.5	388.0	33
V_d(C)	26.7	-9.4	94.6	388.5	54
V_e(C)	8.3	-3.2	95.6	372.5	83
V_f(C)	10.7	-4.1	95.6	372.0	73
VI_a	73.0	3.0	81.2	422.5	49
VI_b	77.3	-6.9	89.3	426.0	39
VI_c	39.2	-10.7	92.2	398.0	32
VI_d	52.4	-12.3	87.2	400.5	52
VI_e	26.7	-4.6	89.0	386.0	89
VI_f	22.0	-6.5	96.6	370.0	36

^a(H): Polyimides were obtained by the thermal imidization method. (C): Polyimides were obtained by the chemical imidization method with DMAc as solvent. ^bThe color parameters were calculated according to a CIE LAB equation, using paper as a standard. L^* is lightness; 100 means white, while 0 implies black. A positive a^* means red color, while a negative a^* indicated green color. A positive b^* means yellow color, while a negative b^* implies blue color.

Table V. Tensile properties of polyimides films

Polymer ^a	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)
V_a	80	71	13	1.7
V_b	—	110	10	2.0
V_c	72	70	37	1.7
V_d	—	83	9	1.7
V_e	—	99	9	1.9
V_f	—	90	8	1.9
VI_a	—	—	—	—
VI_b	—	84	10	1.6
VI_c	—	68	7	1.6
VI_d	—	85	8	1.7
VI_e	98	87	7	2.0
VI_f	93	89	6	2.0

^aPolyimides obtained by the thermal imidization method.

used to evaluate thermal properties of these synthesized polymers. The thermal behavior data of all the fluorinated polymers are presented in Table VI. DSC experiments were conducted at a heating rate of 15 °C/min in nitrogen. Rapid quench-cooling from 400 °C to room temperature produced predominantly amorphous samples, so the glass transition temperatures (T_g) of all the polyimides could be easily discerned in the subsequent heating DSC traces. The T_g values of these polyimides **V_{a-f}** were in the 182–202 °C range, depending on the structure of the dianhydride component and decreasing with the increasing flexibility of the polymer backbones. As expected, the polyimide **V_e** obtained from ODPA showed the lowest T_g due to the presence of a flexible ether linkage between the phthalimide units, and the polyimide

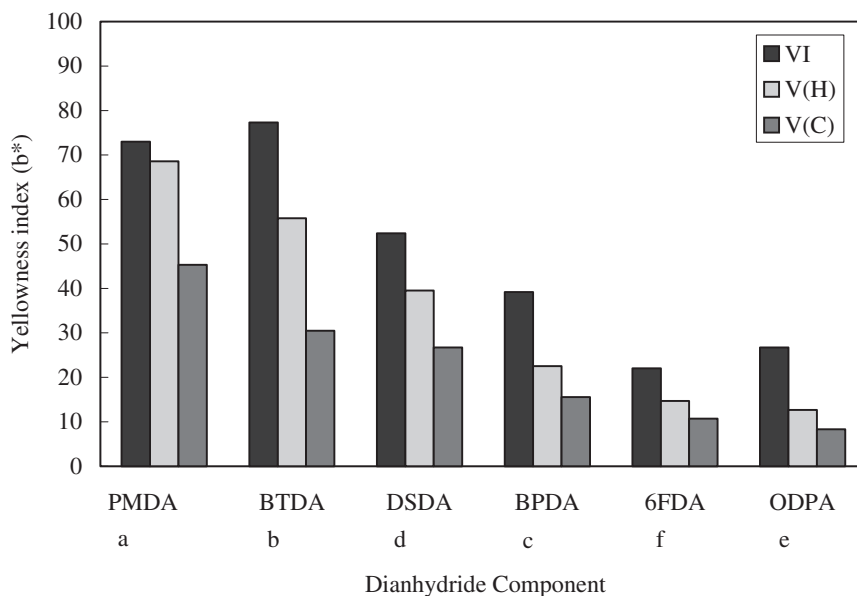
**Figure 7.** Comparison of the yellowness index (b^* value) for PI V and VI.

Table VI. Thermal behavior data of polyimides

Polymer	T_g^a (°C)	$T_{10\% \text{ wt loss}}^b$ (°C)		Char Yield (wt %) ^c
		In N ₂	In Air	
V _a	202	530	525	57
V _b	192	532	532	59
V _c	199	541	535	61
V _d	202	491	495	46
V _e	182	541	537	57
V _f	200	539	529	56
VI _a	248	535	535	47
VI _b	186	532	529	45
VI _c	195	535	536	52
VI _d	197	520	518	55
VI _e	209	509	495	31
VI _f	204	541	536	50

^aThe samples heated from 120 to 400 °C at a scan rate of 20 °C/min; followed by rapid cooling to 120 °C at 100 °C/min in N₂. The midpoint temperature of the baseline shift on the subsequent DSC trace (from 120 to 400 °C at 20 °C/min) was defined as T_g . ^bDecomposition temperature recorded *via* TGA at a heating rate of 20 °C/min and a gas flow rate of 100 cm³/min. ^cResidual weight percentage at 800 °C in nitrogen.

V_a derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit. From the table, the V and VI series have similar T_g s, which indicates that the CF₃ group in the main chain does not affect the T_g of polyimides.

The thermal stability of the polymers was evaluated by TGA at a heating rate of 20 °C/min. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original TGA thermograms and are also tabulated in Table VI. The T_{10} values of V_{a-f} stays within 491–541 °C in nitrogen and within 495–537 °C in air. 45% char yield was found at 800 °C in nitrogen. Polyimides V_d having a sulfonyl group in dianhydride DSDA exhibits lower T_{10} values than the other polyimides. This may be attributed to the weak bonding of C–S bond and easy degradation upon heating. From the result, polyimides V (except for V_d) generally possess higher thermal stability in air than do the VI series. Apparently, the CF₃ group in polymers imparts excellent anti-oxidation properties.

Moisture Absorption Tests. Table VII shows the results of moisture absorption tests. The moisture absorptions of Series-V polyimides are summarized in this table. In comparison, polyimides V_{a-f} exhibit lower moisture absorptions (0.19–0.91%) than do Kapton film (1.84%), owing to the hydrophobicity of the CF₃ group. Moreover, polyimides V_f exhibit the lowest moisture absorption (0.19%) due to their higher fluorine contents in the repeating unit.

Table VII. Moisture absorption of synthesized polyimides

Polyimide ^a	Film Thickness (μm)	Moisture Absorption (%)
V _a	52	0.91
V _b	75	0.29
V _c	87	0.77
V _d	53	0.47
V _e	104	0.31
V _f	75	0.19
General-grade PI (similar to Kapton)	28	1.837

^aPolyimides obtained by the thermal imidization method.

CONCLUSIONS

A colorless, fluorine-containing, crystalline diamine monomer, α, α' -bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,3-diisopropylbenzene (**II**), was first synthesized *via* a high-yield two-step procedure. Then, from this novel monomer (**II**), a series of organo-soluble and light-colored fluorinated polyimides (**V**) were obtained by reacting **II** with various aromatic dianhydrides. The films of ODPDA-derived V_e(C) were found to be almost colorless (b^* value smaller than 9). From this monomer, a series of polyimides were successfully synthesized and extensively characterized in terms of their potential applications. Comparison of chemical cyclodehydration *vs.* thermal cyclodehydration was also done. On the basis of same monomers, the polymers synthesized from the route of chemical cyclodehydration show lighter color (b^* values between 8.3 and 45.3) and better solubility than those produced from the route of thermal cyclodehydration (b^* values between 12.7 and 68.6). By comparisons of polymers of different monomers, Series-V exhibit better solubility, lighter color, and lower moisture absorption than the corresponding non-fluorinated counterpart of polyimides (Series-VI).

It can be concluded that this unique modification approach on the diamine monomer has led to various useful improvements, such as better solubility, good film-forming ability, high optical transparency (λ_o of V(C) are between 372 and 399 nm), excellent thermal stability (10% weight loss at temperature above 490 °C) and low moisture absorption.

REFERENCES

1. "Advances in Polyimide Science and Technology," C. Feger, M. M. Khojasteh, and M. S. Htoo, Ed., Technomic, Lancaster, 1993.
2. "Polyimides and Other High-Temperature Polymers,"

- M. J. M. Abadie and B. Sillion, Ed., Elsevier, Amsterdam, 1991.
3. "Polyimides: Synthesis, Characterization, and Application," Vol. I & II, K. L. Mittal, Ed., Plenum, New York, 1984.
 4. "Polyimides: Materials, Chemistry, and Characterization," C. Feger, M. M. Khojasteh, and J. E. McGrath, Ed., Elsevier, Amsterdam, 1989.
 5. "Polyimide," D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Ed., Black & Son, Glasgow, 1990.
 6. P. E. Cassidy, "Thermally Stable Polymers," Marcel Dekker, New York, 1980.
 7. H. H. Yang, "Aromatic High-Strength Fibers," Wiley, New York, 1989.
 8. a) B. S. Dupont and N. Bilow, U. S. Patent 1986; 4592925.
b) A. L. Landis and A. B. Naselow, U. S. Patent 1987; 4645824.
 9. a) K. Higashi and Y. Noda, Eur. Patent 1986; 240249.
b) S. Tamai, M. Ohta, S. Kawashima, H. Oikawa, K. Ohkoshi, and A. Yamaguchi, Eur. Patent 1987; 234882.
 10. T. Matsuura, S. Ando, S. Sasaki, and F. Yamamoto, *Electron Lett.* **29**, 2107 (1993).
 11. S. Ando, T. Sawada, and Y. Inoue, *Electron. Lett.* **29**, 2143 (1993).
 12. R. A. Dine-Hart and W. W. Wright, *Makromol. Chem.* **143**, 189 (1971).
 13. M. K. Ghosh and K. L. Mittal, "Polyimides: Fundamentals and Applications," Marcel Dekker, New York, 1996.
 14. F. Li, S. Fang, J. J. Ge, P. S. Honigfort, J. C. Chen, F. W. Harris, and S. Z. D. Cheng, *Polymer*, **40**, 4571 (1999).
 15. F. Li, J. J. Ge, P. S. Honigfort, S. Fang, J. C. Chen, F. W. Harris, and S. Z. D. Cheng, *Polymer*, **40**, 4987 (1999).
 16. C. S. Wang and R. W. Yang, *J. Appl. Polym. Sci.*, **66**, 609 (1997).
 17. K. Takashi, S. Atsushi, and T. Shoji, (Mitsui Chemical Industry Co., Japan) Jpn. Kokai Tokkyo Koho JP 2000; 297067, Chem Abstr 2000; 133: 322563h.
 18. K. Takashi, S. Atsushi, and T. Shoji, (Mitsui Chemical Industry Co., Japan) Jpn. Kokai Tokkyo Koho JP 2000; 297153, Chem Abstr 2000; 133: 322280p.
 19. K. Takashi, S. Atsushi, and T. Shoji, (Mitsui Chemical Industry Co., Japan) Jpn. Kokai Tokkyo Koho JP 2000; 297153, Chem Abstr 2000; 133: 310300g.
 20. K. Xie, J. G. Liu, H. W. Zhou, S. Y. Zhang, M. H. He, and S. Y. Yang, *Polymer*, **42**, 7267 (2001).
 21. K. Xie, S. Y. Zhang, J. G. Liu, M. H. He, and S. Y. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 2581 (2001).
 22. S. H. Hsiao, C. P. Yang, and J. C. Fan, *J. Polym. Res.*, **1**, 345 (1994).
 23. W. Yamashita, N. Koga, J. Ookawa, and T. Yamaguchi, Jpn. Kokai Tokkyo Koho JP 1993; 05331282.
 24. M. Mitsuki, K. Yamaguchi, and T. Yamaguchi, Jpn. Kokai Tokkyo Koho JP 1993; 05320100.
 25. C. P. Yang, Y.-P. Chen, and E. M. Woo, *Polymer*, **45**, 5179 (2004).
 26. C. P. Yang, Y.-P. Chen, and E. M. Woo, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 3116 (2004).
 27. C. P. Yang, R. S. Chen, and K. S. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 922 (2003).
 28. C. P. Yang, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3895 (1989).
 29. C. P. Yang, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 1353 (1990).
 30. M. Hasegawa and K. Horie, *Prog. Polym. Sci.*, **26**, 259 (2001).