# Polyimides Based on Aromatic Diisocyanates Containing Pendent Flexible Alkoxy Chains and Aromatic Dianhydrides: Synthesis, Characterization, and Liquid-Crystal Alignment Properties

**Anjana Sarkar, Mahadeo R. Halhalli, Arun D. Kulkarni, Prakash P. Wadgaonkar**

*Polymer Science and Engineering Division, National Chemical Laboratory, Pune 410008, India*

**ABSTRACT:** Four new aromatic diisocyanates containing pendent flexible alkoxy chains, namely, 5-butyloxy-1,3-phenylenediisocyanate, 5-octyloxy-1,3-phenylenediisocyanate, 5-dodecyloxy-1,3-phenylenediisocyanate, and 5-hexadecyloxy-1,3-phenylenediisocyanate, were synthesized by Curtius rearrangement of the corresponding 5-alkoxy-1,3-phenylene diacylazides. These diisocyanates were each polycondensed with three commercially available aromatic dianhydrides: 4,4′-oxydiphthalic anhydride, 3,3′,4,4′-(hexafluoroisopropylidene) diphthalic anhydride, and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride—in benzonitrile in the presence of 1,4-diazabicyclo[2.2.2]octane as a catalyst to obtain a series of polyimides with inherent viscosities in the range 0.16–0.43 dL/g. Except for 3,3′,4,4′-benzophenonetetracarboxylic dianhydride based polyimides, all of the polyimides were found to be soluble in dichloromethane, *m*-cresol, 1-methyl-2-pyrrolidinone, tetra-chloroethane, and pyridine either at room temperature or on heating and could be cast into tough, flexible, transparent films from a solution in *m*-cresol or tetrachloroethane. X-ray diffractograms revealed that the polyimides with longer alkoxy chains had layered structures. The glass-transition temperature of the polyimides containing pendent flexible alkoxy chains were in the range 159–246°C as measured by differential scanning calorimetry. The temperature for the 10% weight loss of the polyimides was in the range 410–460°C in a nitrogen atmosphere, which indicated good thermal stability. A pretilt angle of 2.97° was observed for the polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and 4,4′-oxydiphthalic anhydride. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 461–472, 2009

**Key words:** high performance polymers; polyimides; thermal properties

## INTRODUCTION

Polyimides exhibit excellent thermal and mechanical properties and have extensive engineering and microelectronics applications.[1] Because conventional aromatic polyimides are insoluble, these polymers are usually processed as the corresponding soluble poly(amic acid) precursors and then either thermally or chemically imidized. However, there are some problems because of the instability of poly(amic acid)s and the liberation of water in the imidization process. Therefore, soluble polyimides that can be easily processed are desired. There are several approaches that have been tried with varying degrees of success to improve the solubility/processability of aromatic polyimides.[2–6] The attachment of flexible side chains has drawn particular interest in polyimide synthesis because it increases not only the processability of polyimides but also the pretilt angle of liquid-crystal molecules on rubbed polymer surfaces.[7–9] Considering the two most routinely practiced routes for the synthesis of polyimides, namely, the diamine–dianhydride reaction and the diisocyanate–dianhydride reaction, three options are available for attaching flexible side chains to aromatic polyimides. These are (1) diamine modification,[10–12] (2) dianhydride modification,[9] and (3) diisocyanate modification.[13–18]

The purpose of this study was to synthesize aromatic polyimides based on meta-oriented aromatic diisocyanates containing pendent flexible alkoxy chains of various carbon lengths by polycondensation with commercially available aromatic dianhydrides and to study the effect of pendent flexible alkoxy chains on the properties of the resulting polyimides. 5-Alkoxy-1,3-phenylenediisocyanates, namely, 5-butyloxy-1,3-phenylenediisocyanate (BPDC), 5-octyloxy-1,3-phenylenediisocyanate (OPDC), 5-dodecyloxy-1,3-phenylenediisocyanate (DDPDC), and 5-hexadecyloxy-1,3-phenylenediisocyanate (HDPDC), were synthesized and polycondensed with aromatic dianhydrides, namely, 4,4′-oxydiphthalic anhydride (ODPA), 3,3′,4,4′-(hexafluoroisopropylidene) diphthalic anhydride (FDA), and 3,3′,4,4′-benzophenonetetracarboxylic

dianhydride (BTDA) in benzonitrile in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), as catalyst to obtain a series of polyimides. Polyimides were characterized by inherent viscosity measurements, IR and NMR spectroscopy, solubility tests, X-ray diffraction studies, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The polyimide derived from OPDC and ODPA was evaluated for its liquid-crystal alignment properties.

## EXPERIMENTAL

### Materials

5-Hydroxyisophthalic acid, 1-bromobutane, 1-bromooctane, 1-bromododecane, and 1-bromohexadecane (Sigma–Aldrich Chemicals, St. Louis, MO) were used as received. The dianhydrides, ODPA, FDA, and BTDA (Aldrich), were sublimed under reduced pressure before use. Toluene and n-hexane (Merck Chemicals, Darmstadt, Germany) were dried over sodium and calcium hydride, respectively, and distilled before use. Benzonitrile was dried over phosphorous pentoxide for 12 h and then distilled under reduced pressure before use. Triethylamine, ethylchloroformate, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), tetrachloroethane (TCE), dimethyl sulfoxide, pyridine, dichloromethane (DCM), chloroform, and m-cresol were reagent grade and were purified as per literature procedures.[19] Sodium azide was activated by trituration with hydrazine hydrate and left overnight. It was dissolved in a minimum quantity of water and precipitated with acetone, filtered, and dried in a vacuum oven at room temperature. DABCO was recrystallized from pet ether and dried under reduced pressure at 50°C. The 5-alkoxyisophthalic acids were synthesized from 5-hydroxyisophthalic acid as described in the literature.[20]

### Measurements

Inherent viscosity measurements were made with a 0.5% (w/v) solution of polyimides either in m-cresol or concentrated sulfuric acid at 30 ± 0.1°C with an Ubbelohde suspended-level viscometer (State College, PA). IR spectra were recorded with polyimide films or powders on a PerkinElmer 599B spectrophotometer (Waltham, MA). $^1$H-NMR spectra were recorded on a Bruker NMR spectrometer (200 or 500 MHz, Billerica, MA) at room temperature with $CDCl_3$ as the solvent. The solubility of the polyimides was determined at a 3 wt % concentration in various solvents at room temperature or on heating. TGAs were performed on PerkinElmer TGA-7 analyzer at a heating rate of 10°C/min under a nitrogen atmosphere. DSC analysis was performed on Perkin-

Elmer DSC-7 at a heating rate of 40°C/min under a nitrogen atmosphere. X-ray diffractograms of the polyimides were obtained on a Rigaku Dmax 2500 X-ray diffractometer (Tokyo, Japan).

### Cell preparation for pretilt angle measurements

Indium tin oxide (ITO) coated glass (25 × 25 $mm^2$) was obtained from M/s Merck, Ltd. (Darmstadt, Germany). The ITO-coated glass substrate was thoroughly washed successively with soap solution, deionized water, and ethanol and then dried. A 1 wt % solution of the polyimide obtained by the polycondensation of OPDC with ODPA (PI-2) was prepared in TCE by heating. The spin coating of the polyimide was performed with a Karl Süss CT-62 spin coater (Decatur, GA) (5 s at 1000 rpm, 40 s at 5000 rpm) on the ITO side. After spin coating, the substrate was preheated at 100°C for 10 min.

The liquid crystal E7, a mixture consisting of 50.6% 4′-pentylcyanobiphenyl (5CB), 25.2% 4′-heptylcyanobiphenyl, 17.8% 4′-octyloxycyanobiphenyl, and 6.4% 4′-pentylcyanoterphenyl ([nematic–isotropic temperature = 60°C, density = 1.06 g/$cm^3$, $\varepsilon_{\parallel} = 19$, $\varepsilon_{\perp} = 5.2$, and $\Delta\eta = 0.225$ (where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are dielectric constants, along the local director **n** and normal to director **n**, respectively, $\Delta\eta$ is difference in the indices of refraction)]) was obtained from M/s Merck.

Electro-optical cells were constructed with ITO-coated glass coated with the polyimide substrate. The polyimide surface was rubbed uniformly with a velvet cloth. A twisted nematic cell was constructed by the placement of the two substrates orthogonal to each other with respect to their rubbing direction. The cells were secured with UV curable glue (Norland UV Sealant 91, Cranbury, NJ) with 18-μm spacers. The cells were filled with the liquid-crystal material E7 by capillary action at 80°C, which was 20°C above the nematic–isotropic transition temperature of the liquid crystal.

Electro-optical characteristics were investigated with a DMS 703 display measuring system (Autronic-Melchers GmbH, Karlsruhe, Germany). A square wave was used to drive the cells for the dynamic response measurements at 1000 Hz. The pretilt angle was measured directly with the crystal rotation method (Autronic, TBA 107, Karlsruhe, Germany).[21]

### Synthesis of the diisocyanates

Synthesis of the 5-alkoxyisophthaloyl diazides

A representative procedure for the synthesis of the 5-alkoxyisophthaloyl diazides is described. Into a 100-mL, two-necked, round-bottom flask equipped with an addition funnel and a thermowell were placed 5-hexadecyloxyisophthalic acid (1 g, 2.5 mmol) and a mixture of THF and water (3 : 1 v/v, 7 mL). The reaction mixture was cooled to 0°C, and a solution of triethylamine (0.74 g, 7.3 mmol) in THF
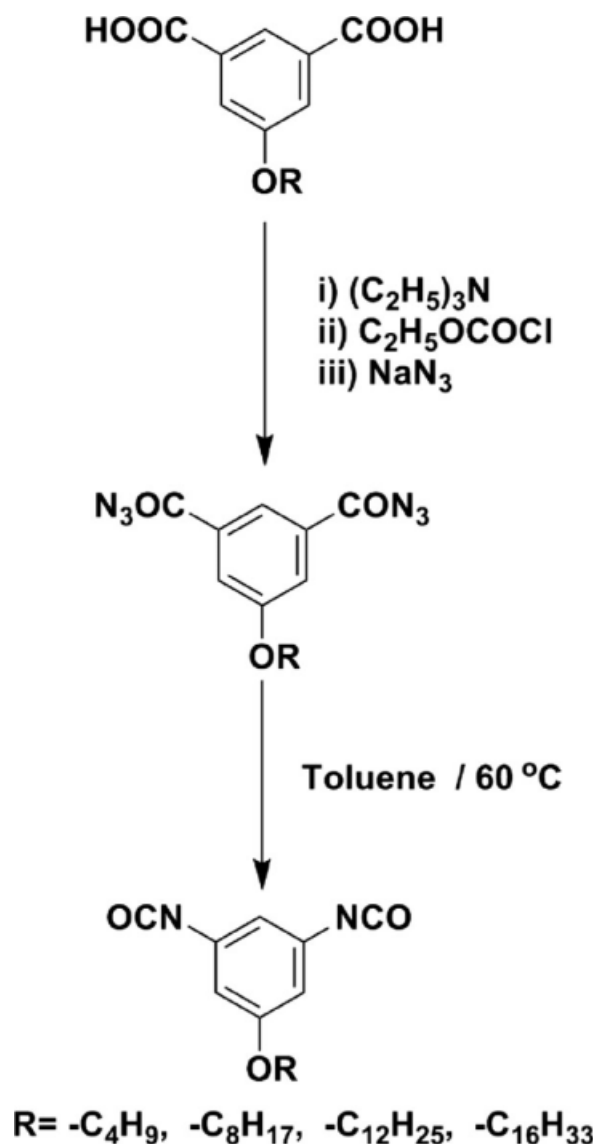
**Scheme 1** Synthesis of 5-alkoxy-1,3-phenylenediiso-cyanates.

(3 mL) was added dropwise over a period of 15 min. To the clear solution formed was added ethylchloroformate (0.79 g, 7.3 mmol) dropwise over a period of 10 min, and the reaction mixture was stirred for 2 h. A solution of activated sodium azide (0.63 g, 9.7 mmol) in water (5 mL) was added dropwise over a period of 15 min, and the reaction mixture was stirred at 0°C for 4 h. Cold water (50 mL) was added gradually to the reaction mixture, and the solid that separated out was collected by filtration and washed with cold water (2 × 25 mL). The product was dissolved in DCM (25 mL), dried over anhydrous sodium sulfate, and filtered, and DCM was removed under reduced pressure at room temperature to obtain a white solid (yield = 1.02 g, 91%).

Synthesis of the 5-alkoxy-1,3-phenylenediisocyanates

A representative procedure for the synthesis of the 5-alkoxy-1,3-phenylenediisocyanates is described. Into a 100-mL, three-necked, round-bottom flask equipped with a nitrogen inlet tube and a reflux condenser were placed 5-hexadecyloxyisophthaloyl diazide (1.0 g, 2.2 mmol) and dry toluene (20 mL). Nitrogen gas was bubbled gently through the reaction mixture. The reaction mixture was heated at 60°C for 24 h. The evaporation of toluene under reduced pressure afforded a crude product. Crystallization of the crude diisocyanate from dry hexane yielded HDPDC in pure form (yield = 0.72 g, 82%).

**Synthesis of the polyimides**

A representative procedure for the synthesis of the polyimides is described. Into a 25-mL, two-necked, round-bottom flask equipped with a nitrogen inlet and a reflux condenser were placed HDPDC (0.44 g, 1.1 mmol), ODPA (0.34 g, 1.1 mmol), DABCO (0.043 g, 0.37 mmol), and benzonitrile (3.5 mL). The

**TABLE I**
**Physical and Spectral Characterization Data for 5-Alkoxyisophthaloyl Diazides**

| No. | Diacyl azide | Yield (%) | mp (°C) | IR (cm$^{-1}$) | $^1$H-NMR ($\delta$, ppm, CDCl$_3$) |
|---|---|---|---|---|---|
| 1 | BIDAz | 98 | 42–43 | 2148 (—N$_3$), 1690 (—C=O), 1230 (Ar—O—C) | 0.97 (3H, t, —CH$_3$), 1.40–1.66 (2H, m, —CH$_2$), 1.66–1.90 (2H, m, —CH$_2$), 4.02 (2H, t, —OCH$_2$), 7.74 (2H, s, ArH ortho to ether), 8.19 (1H, s, ArH para to ether) |
| 2 | OIDAz | 98 | 49 | 2148 (—N$_3$), 1690 (—C=O), 1230 (Ar—O—C) | 0.90 (3H, t, —CH$_3$), 1.15–1.58 (10H, m, —CH$_2$), 1.73–1.90 (2H, m, —CH$_2$), 4.02 (2H, t, —OCH$_2$), 7.74 (2H, s, ArH ortho to ether), 8.19 (1H, s, ArH para to ether) |
| 3 | DDIDAz | 96 | 57 | 2148 (—N$_3$), 1690 (—C=O), 1230 (Ar—O—C) | 0.90 (3H, t, —CH$_3$), 1.15–1.58 (18H, m, —CH$_2$), 1.74–1.90 (2H, m, —CH$_2$), 4.02 (2H, t, —OCH$_2$), 7.75 (2H, s, ArH ortho to ether), 8.20 (1H, s ArH para to ether) |
| 4 | HDIDAz | 91 | 68 | 2148 (—N$_3$), 1690 (—C=O), 1230 (Ar—O—C) | 0.89 (3H, t, —CH$_3$), 1.14–1.58 (26H, m, —CH$_2$), 1.74–1.92 (2H, m, —CH$_2$), 4.02 (2H, t, —OCH$_2$), 7.74 (2H, s, ArH ortho to ether), 8.19 (1H, s, ArH para to ether) |

BIDAz = 5-butyloxyisophthaloyl diazide; DDIDAz = 5-dodecyloxyisophthaloyl diazide; HDIDAz = 5-hexadecyloxyisophthaloyl diazide; OIDAz = 5-octyloxyisophthaloyl diazide.

**TABLE II**
**Physical and Spectral Characterization Data for 5-Alkoxy-1,3-phenylenediisocyanates**

| No. | Diisocyanate | Yield (%) | mp (°C)/bp (°C/mmHg) | IR (cm$^{-1}$) | $^1$H-NMR ($\delta$, ppm, CDCl$_3$) |
|-----|--------------|-----------|----------------------|----------------|-------------------------------------|
| 1 | BPDC | 89 | 199/10$^{-3}$ | 2256 (N=C=O), 1214 (Ar—O—C) | 0.97 (3H, t, —CH$_3$), 1.40–1.60 (2H, m, —CH$_2$), 1.65–1.80 (2H, m, —CH$_2$), 3.90 (2H, t, —OCH$_2$), 6.40 (1H, s, ArH para to ether), 6.45 (2H, s, ArH ortho to ether) |
| 2 | OPDC | 88 | 210/10$^{-3}$ | 2256 (N=C=O), 1216 (Ar—O—C) | 0.90 (3H, t, —CH$_3$), 1.12–1.55 (10H, m, —CH$_2$), 1.65–1.90 (2H, m, —CH$_2$), 3.89 (2H, t, —OCH$_2$), 6.41 (1H, s, ArH para to ether), 6.45 (2H, s, ArH ortho to ether) |
| 3 | DDPDC | 87 | 50 | 2258 (N=C=O), 1214 (Ar—O—C) | 0.87 (3H, t, —CH$_3$), 1.12–1.55 (18H, m, —CH$_2$), 1.65–1.90 (2H, m, —CH$_2$), 3.89 (2H, t, —OCH$_2$), 6.41 (1H, s, ArH para to ether), 6.45 (2H, s, ArH ortho to ether) |
| 4 | HDPDC | 82 | 66–67 | 2262 (N=C=O), 1214 (Ar—O—C) | 0.87 (3H, t, —CH$_3$), 1.12–1.55 (26H, m, —CH$_2$), 1.67–1.92 (2H, m, —CH$_2$), 3.89 (2H, t, —OCH$_2$), 6.40 (1H, s, ArH para to ether), 6.44 (2H, s, ArH ortho to ether) |

reaction mixture was stirred at 140°C under a nitrogen atmosphere for 10 h. At the end of the reaction time, the reaction mixture was poured into excess methanol. The precipitated polymer was collected by filtration at a pump; this was followed by thorough washing with hot methanol. The polymer was dried at 120°C for 12 h under reduced pressure.

## RESULTS AND DISCUSSION

### Synthesis of the diisocyanates

Diisocyanates are used for the synthesis of a host of thermally stable polymers, such as polyimides, polyamides, poly(amide imide)s, and polyhydantoins. Diisocyanates can be synthesized by a variety of methods, of which the phosgenation of diamines and Curtius rearrangement of diacylazides to diisocyanates are important.

In this study, a series of aromatic meta-oriented diisocyanates containing pendent flexible alkoxy chains was synthesized with the Curtius rearrangement reaction (Scheme 1). 5-Alkoxyisophthalic acids were conveniently prepared from commercially available 5-hydroxyisophthalic acid.[20] The diacylazides were prepared from 5-alkoxyisophthalic acids by the elegant one-pot Weinstock modification of the Curtius reaction. The diacids were successively treated with triethylamine, ethylchloroformate, and sodium azide. The reaction of a diacid with triethylamine produces a salt, which, on treatment with ethylchloroformate, results in the formation of mixed carboxylic–carbonic anhydride. In the reaction of the mixed carboxylic–carbonic anhydride, the azide ion attacks the more electrophilic carbonyl group, which results in the formation of the acylazide. The reaction conditions used were mild, and there were apparently no side products formed in this one-pot
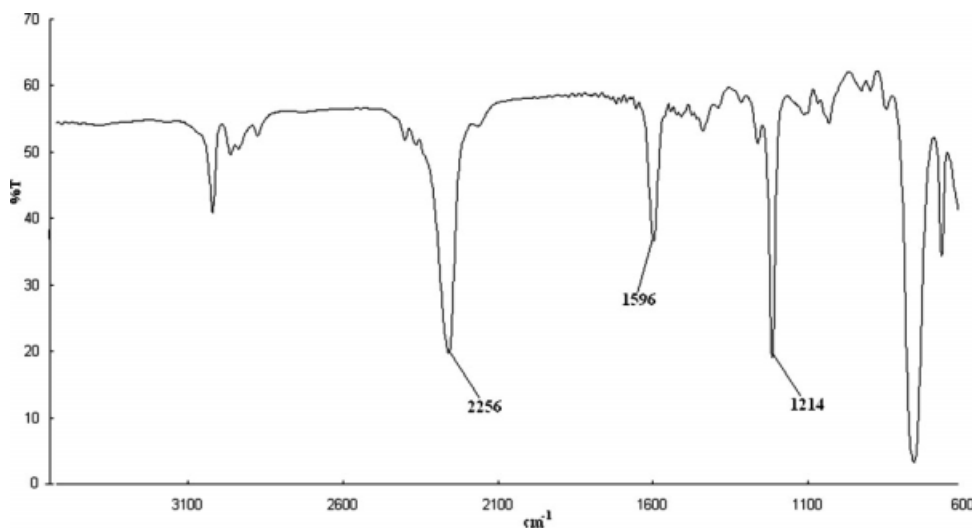


**Figure 1**   IR spectrum of BPDC in CHCl$_3$.

reaction. The diacyl azides were dissolved in dry toluene and decomposed by heating at 60°C to give the corresponding diisocyanates. Purification of the crude diisocyanates was achieved by either distillation under reduced pressure or crystallization from dry hexane.

The diacylazides and diisocyanates were characterized by IR and $^1$H-NMR spectroscopy. The spectral data of the diacylazides and diisocyanates are shown in Tables I and II, respectively. The IR spectra of all of the diacylazides showed strong absorption bands at 2148 cm$^{-1}$ due to the asymmetric stretching
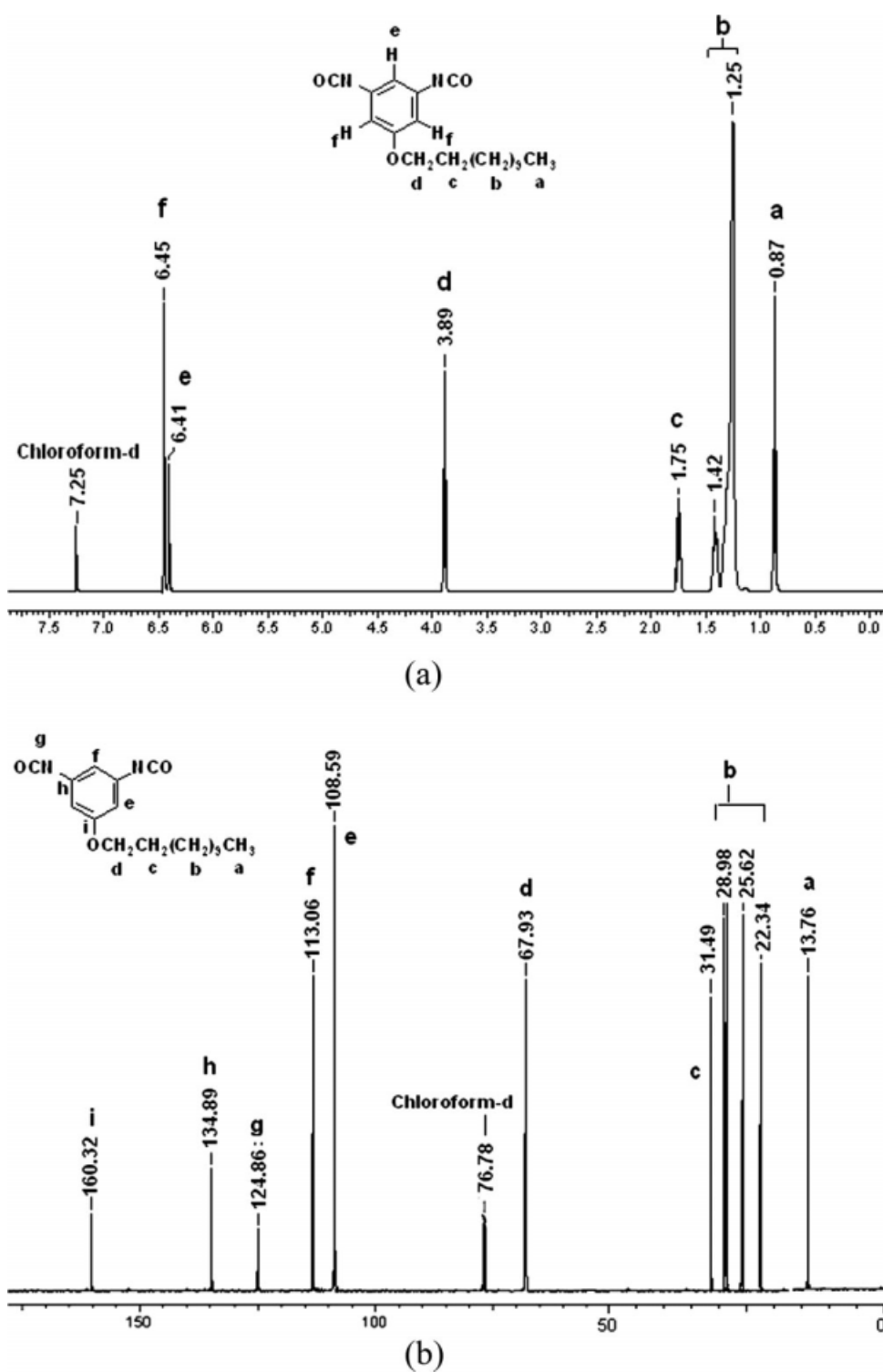


**Figure 2** (a) $^1$H-NMR and (b) $^{13}$C-NMR spectra of DDPDC in CDCl$_3$.

vibration of the $-N_3$ group and bands at 1690 cm$^{-1}$ corresponding to the carbonyl of the azido carbonyl group. A representative IR spectrum of BPDC is shown in Figure 1, which showed bands at 2256 and 1214 cm$^{-1}$ corresponding to N=C=O and C—O—C stretching vibrations, respectively.

The $^1$H-NMR spectrum of DDPDC [Fig. 2(a)] was in accordance with the structure proposed. The aromatic protons ortho to the ether linkage appeared as a singlet at 6.45 δ ppm, whereas the aromatic proton flanked by isocyanate groups exhibited a singlet at 6.41 δ ppm. The upfield chemical shift of the aromatic protons in the diisocyanate was likely due to a combination of a mesomeric effect of ether oxygen and shielding due to neighboring group anisotropy of the isocyanate group. The dominating effect appeared to be the mesomeric effect of the ether linkage. The methylene protons α and β to the oxygen atom appeared as a triplet at 3.89 δ ppm and as a multiplet in the range 1.65–1.90 δ ppm, respectively. The other methylene protons displayed multiplets centered at 1.42 and 1.25 δ ppm. The methyl protons of the aliphatic chain appeared as a triplet at 0.87 δ ppm.

The $^{13}$C-NMR spectrum of 5-dodecyloxy-1,3-phenylenediisocyanate, along with assignments of the carbon atoms, is shown in Figure 2(b). In the $^{13}$C-NMR spectrum of diisocyanate, the chemical shift at 125 ppm was assigned to the carbon atom of the NCO group (on the basis of the assignment of the carbon atom of the NCO group in phenyl isocyanate).

## Synthesis of the polyimides

We synthesized the polyimides by the reaction of stoichiometric quantities of the diisocyanates and dianhydrides in benzonitrile in the presence of DABCO as a catalyst (Scheme 2) following the procedure reported by Imai et al.[22] The diisocyanate–dianhydride reaction proceeded via the formation of a seven-membered cyclic intermediate, which decomposed on heating to form a polyimide with the evolution of carbon dioxide.[23] In synthesis of the polyimides from both ODPA and FDA, the reaction mixture was homogeneous throughout the course of polymerization, whereas in the case of BTDA, the reaction mixture became heterogeneous because of the precipitation of the formed polyimide. The inherent viscosities of the polyimides were in the range 0.27–0.43 dL/g for the ODPA- and FDA-based polyimides containing pendent alkoxy group, which indicated the formation of low to medium molecular weight polymers. BTDA-derived polyimides precipitated out of the reaction mixture and, consequently, showed lower inherent viscosities, which were in the range 0.16–0.19 dL/g (Table III).
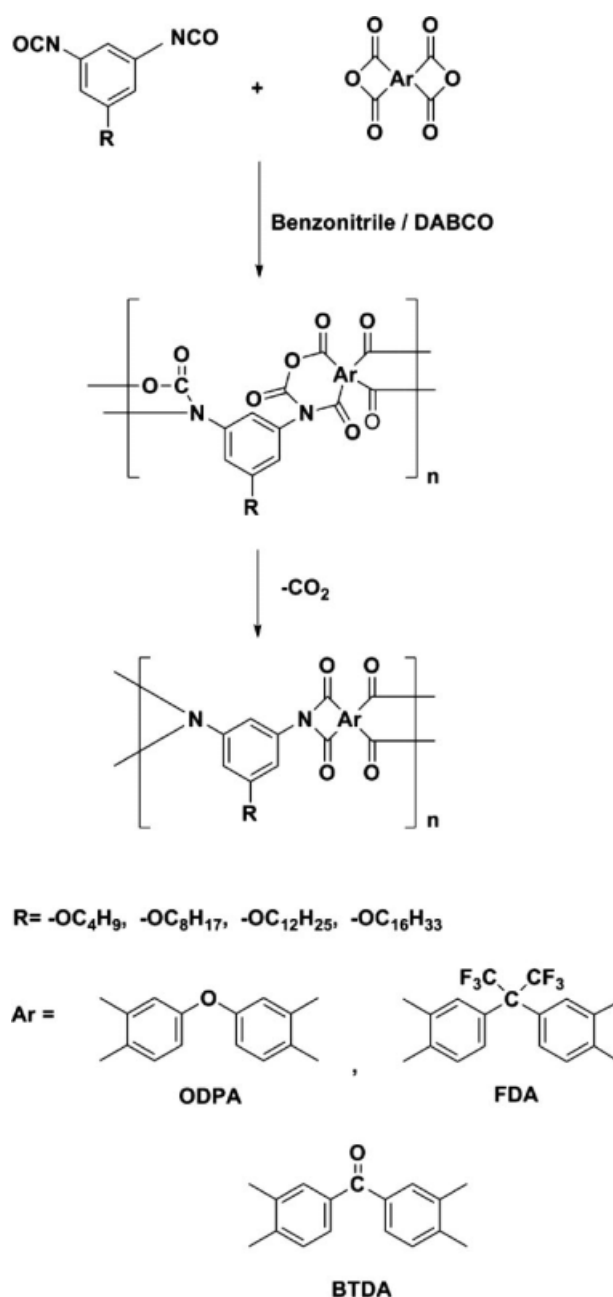


**Scheme 2** Synthesis of aromatic polyimides from 5-alkoxy-1,3-phenylenediisocyanates and aromatic dianhydrides.

## Polymer characterization

The formation of the polyimides was confirmed by IR and NMR spectroscopy. A representative IR spectrum of the polyimide derived from HDPDC and ODPA is shown in Figure 3. Absorption bands at 1780 and 1720 cm$^{-1}$ (imide I), 1354 cm$^{-1}$ (imide II), 1142 cm$^{-1}$ (imide III), and 746 cm$^{-1}$ (imide IV) were observed. The imide I band was attributed to the stretching vibration of the two carbonyl groups, which were weakly coupled. The imide II, III, and IV bands were assigned, respectively, to the axial,

**TABLE III**
**Synthesis of Aromatic Polyimides Based on 5-Alkoxy-1,3-phenylenediisocyanates and Aromatic Dianhydrides**

| Polyimide | Diisocyanate (—R substituent) | Dianhydride | Inherent viscosity (dL/g) | $T_g$ (°C) | TGA | |
| | | | | | IDT (°C) | $T_{10}$ (°C) |
|---|---|---|---|---|---|---|
| PI-1 | —OC$_4$H$_9$ | ODPA | 0.42[a] | 237 | 440 | 460 |
| PI-2 | —OC$_8$H$_{17}$ | ODPA | 0.42[a] | 185 | 440 | 455 |
| PI-3 | —OC$_{12}$H$_{25}$ | ODPA | 0.35[a] | 162 | 435 | 445 |
| PI-4 | —OC$_{16}$H$_{33}$ | ODPA | 0.36[a] | 159 | 435 | 445 |
| PI-5 | —OC$_4$H$_9$ | FDA | 0.41[a] | 246 | 390 | 410 |
| PI-6 | —OC$_8$H$_{17}$ | FDA | 0.43[a] | 195 | 420 | 430 |
| PI-7 | —OC$_{12}$H$_{25}$ | FDA | 0.29[a] | 165 | 440 | 450 |
| PI-8 | —OC$_{16}$H$_{33}$ | FDA | 0.27[a] | 161 | 415 | 425 |
| PI-9 | —OC$_4$H$_9$ | BTDA | 0.18[b] | 244 | 420 | 450 |
| PI-10 | —OC$_8$H$_{17}$ | BTDA | 0.19[b] | 195 | 420 | 440 |
| PI-11 | —OC$_{12}$H$_{25}$ | BTDA | 0.16[b] | 182 | 410 | 440 |
| PI-12 | —OC$_{16}$H$_{33}$ | BTDA | 0.18[b] | 179 | 415 | 445 |

IDT = initial decomposition temperature; $T_{10}$ = temperature at which a 10% weight loss was observed.
[a] The inherent viscosity of the polyimide was measured at a concentration of 0.5 g/dL in *m*-cresol at 30 ± 0.1°C.
[b] The inherent viscosity of the polyimide was measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 ± 0.1°C.

transverse, and out-of-plane vibrations of the cyclic imide structure.

The $^1$H-NMR spectrum, along with the assignments of the polyimide derived from 5-butyloxy-1,3-phenylenediisocyanate and FDA (PI-5) recorded in CDCl$_3$, is shown in Figure 4(a). Protons ortho to the imide ring appeared as a doublet at 8.05 δ ppm. Protons flanked by the imide ring and the hexafluoroisopropylidene group showed a singlet at 7.95 δ ppm, whereas the protons ortho to hexafluoroisopropylidene group appeared as a doublet at 7.87 δ ppm. The proton para to the ether linkage appeared as a singlet at 7.20 δ ppm, whereas two aromatic protons ortho to the ether linkage exhibited a singlet at 7.06 δ ppm. The methylene protons attached to the ether linkage showed a triplet at 4.0 δ ppm. The protons attached to the carbons β and γ to the ether oxygen each showed multiplets centered at 1.78 and

1.45 δ ppm, respectively. The methyl protons appeared as a triplet at 0.95 δ ppm.

The $^{13}$C-NMR spectrum of the polyimide derived from BPDC and FDA is shown in Figure 4(b) along with assignments of the carbon atoms. The carbon atoms attached to fluorine showed four characteristic peaks at 119.61, 121.89, 124.19, and 126.47 δ ppm. The imide carbonyls showed two peaks at 165.34 and 165.18 δ ppm. The downfield chemical shift was due to the electron-withdrawing characteristics of the oxygen atom.

## Polymer solubility

The polyimides were tested for solubility (3 wt %) in different solvents. The polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and FDA were soluble in DCM, TCE, DMF, DMAc, NMP, *m*-cresol,
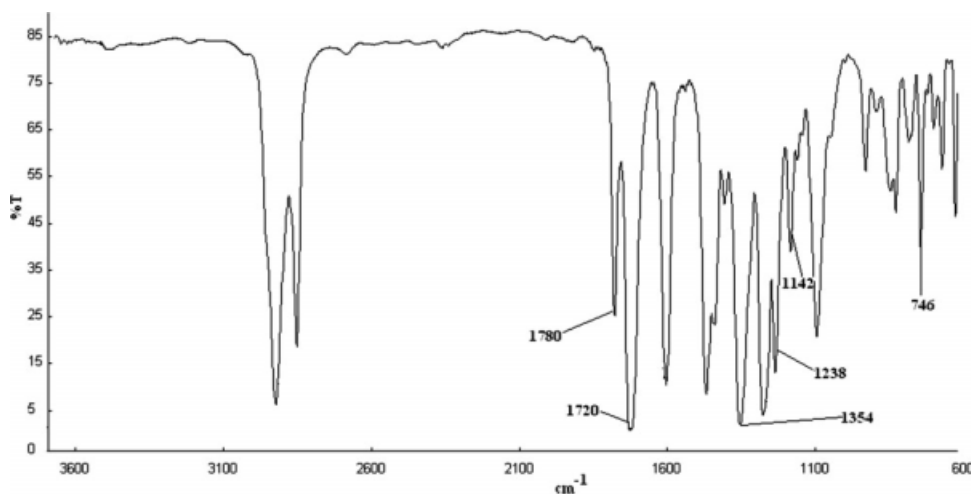


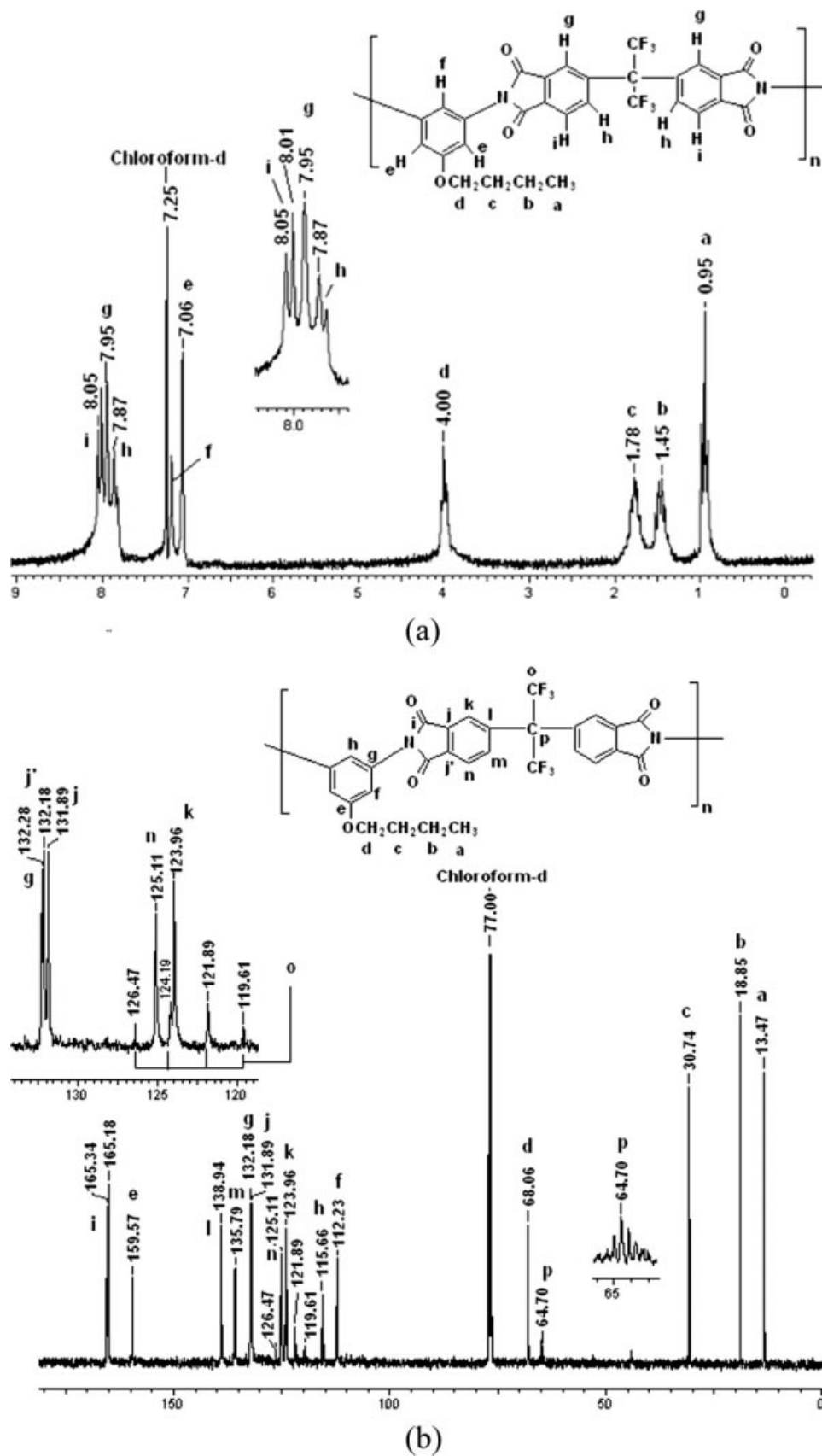**Figure 3** IR spectrum (film) of a polyimide derived from HDPDC and ODPA.

**Figure 4** (a) $^1$H-NMR and (b) $^{13}$C-NMR spectra of a polyimide derived from BPDC and FDA in CDCl$_3$.

and pyridine. The solubility of the polyimides based on FDA was attributed to the low cohesive energy provided by the fluorinated groups and the reduction in charge-transfer complexes of a conjugated aromatic system.[24] The polyimide derived from FDA and *m*-phenylene diamine (an analogous polyimide without a pendent side chain) was also reported to be soluble in solvents such as DMF, DMAc, and NMP at room temperature.[25] Therefore, the unequivocal role of the pendent alkoxy chain for the improvement of the solubility of FDA-based polyimides could not be confirmed on the basis of the solubility data.

The polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and ODPA were soluble in *m*-cresol, NMP, pyridine, and TCE upon heating. The polyimide derived from *m*-phenylene diamine and ODPA—the control polyimide without a pendent alkoxy chain—was reported to swell in *m*-cresol.[25,26] Nonetheless, the improvement in the solubility of this series of ODPA-based polyimides was attributed to the entropy effect of the flexible alkoxy groups.

The polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and BTDA were partially soluble in *m*-cresol and NMP and were insoluble in DMF, DMAc, TCE, and pyridine. Because of the relatively rigid BTDA moiety as compared to the ODPA moiety, the BTDA-derived polyimides were insoluble. Thus, the solubility of the polyimides was governed by both the dianhydride and the diisocyanate structure, with the former having a greater influence.
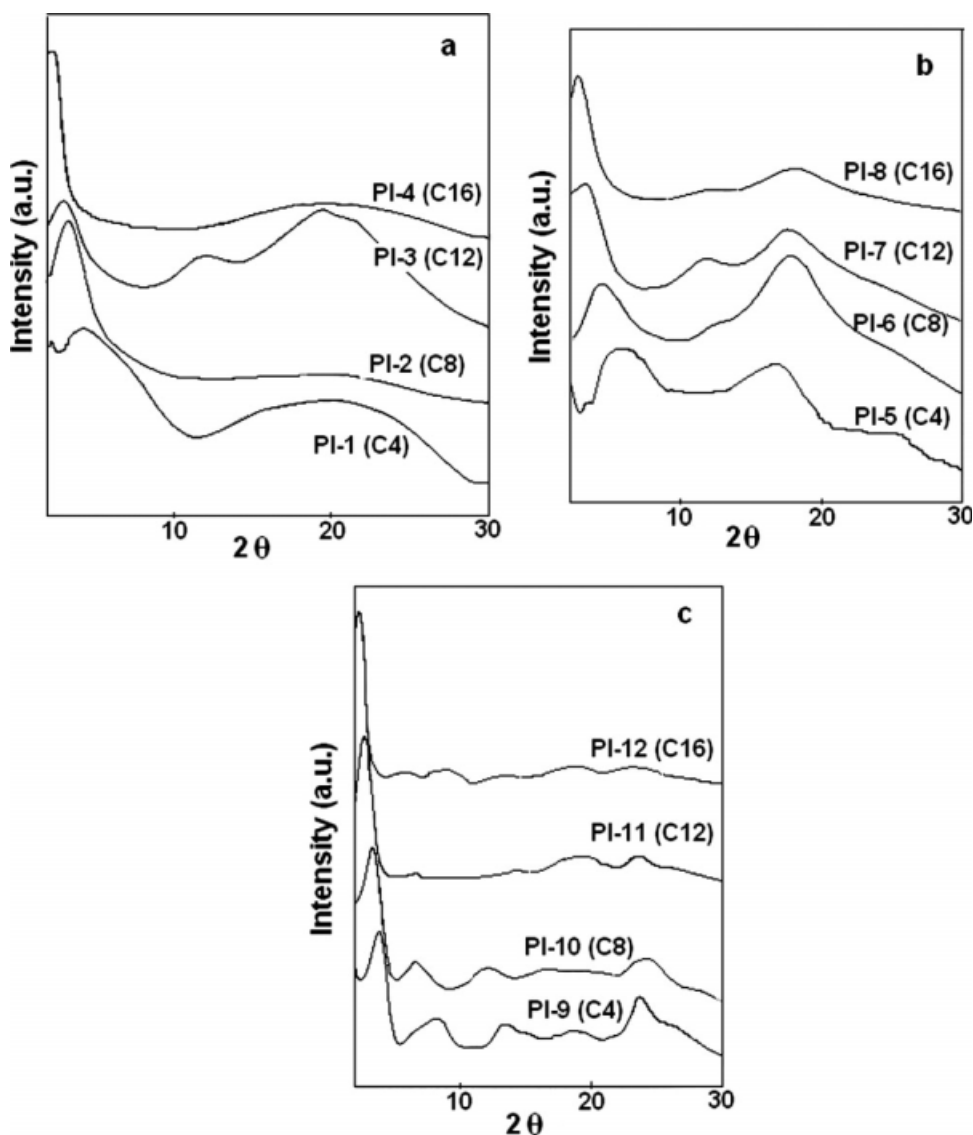


**Figure 5** X-ray diffractograms of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and (a) ODPA (PI-1 to PI-4), (b) FDA (PI-5 to PI-8), and (c) BTDA (PI-9 to PI-12).
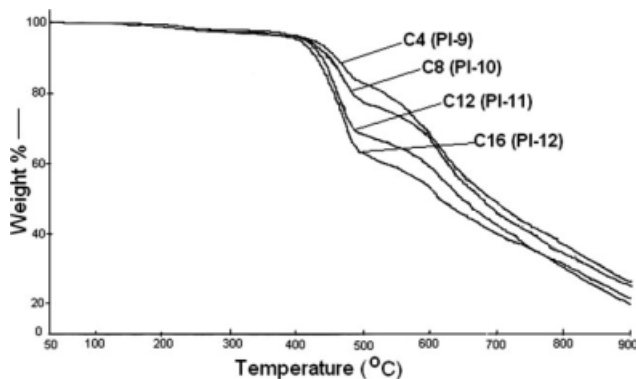
**Figure 6** TG curves of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and BTDA (PI-9 to PI-12).

## X-ray diffraction studies

The wide-angle X-ray diffractograms of the polyimides derived from ODPA and FDA (Fig. 5) showed a broad peak at about $2\theta = 19°$ in the wide-angle region. These peaks were so broad that they could be considered amorphous halos. On the other hand, the BTDA-based polyimides exhibited recognizable peaks near $2\theta$ values of 5, 12, 19, and 24°. This means that the BTDA-based polyimides were partially crystalline in nature, which was also reflected in their poorer solubility as compared to the ODPA- and FDA-based polyimides. The X-ray diffractograms also showed a distinct peak in the middle-angle region ($2\theta = 2$–6°) for all of the polyimides containing pendent alkoxy chains. This peak shifted to smaller angles and its intensity increased as the side-chain length increased. These peaks were characteristic of a typical layered structure resulting from the ordered packing of the aliphatic side chains. These layered structures develop more tightly with increasing side-chain length, which may be attributed to the fact that longer aliphatic side chains facilitate better packing of polymer chains. A similar type of behavior with polyamideimides containing pendent alkoxy groups was reported by our group.[27,28] Such observations have also been reported for rigid rod polymers with long flexible side chains.[29–33]

## Thermal properties

The thermal stability of the polyimides with alkoxy side chains was investigated by TGA at a heating rate of 10°C/min in nitrogen. The thermal degradation of the polyimides began in the temperature range 390–440°C and showed a stepwise degradation with increasing temperature. The initial decomposition temperature of the polyimides containing pendent alkoxy chains were lower than that of analogous polyimides without alkoxy side chains, which were

reported to be stable up to 540–547°C.[32] The degradation occurring in the first step was attributed to the decomposition of the labile alkyl group, with cleavage occurring at the alkyl–ether bond. The weight loss in the first degradation step increased with increasing side-chain length, as shown from the representative thermogravimetry (TG) curves (Fig. 6). The temperature at the second maximum degradation (620°C) corresponded to the thermal scission of the polyimide backbone. This temperature was comparable to the maximum degradation temperature for aromatic polyimides, which implied that backbone of the polyimide containing the pendent alkoxy chains was mostly maintained, even after the scission of the side chains.

The glass-transition temperatures ($T_g$'s) of the polyimides were measured by DSC. $T_g$ values were obtained from second heating scans of the polyimide samples, and the values are shown in Table III. The $T_g$ values of the polyimides were in the range 159–246°C. A plot of $T_g$ versus the number of carbon atoms in the pendent alkoxy chains of the polyimides derived from the 5-alkoxy-1,3-phenylenediisocyanates and aromatic dianhydrides is shown in Figure 7. The $T_g$ values for the reference polyimides derived from *m*-phenylene diamine and the respective dianhydrides—analogous polyimides without pendent alkoxy chains—were taken from the literature.[26] The $T_g$ values of the polyimides containing pendent flexible alkoxy groups were lower than those of the reference polyimides. The depression of $T_g$ values with increasing side-chain length indicated that the side chains acted on the main chains as bound solvents or internal plasticizers. The effect of the alkoxy chain in lowering the $T_g$ value was pronounced up to a chain length of 12 carbon atoms.
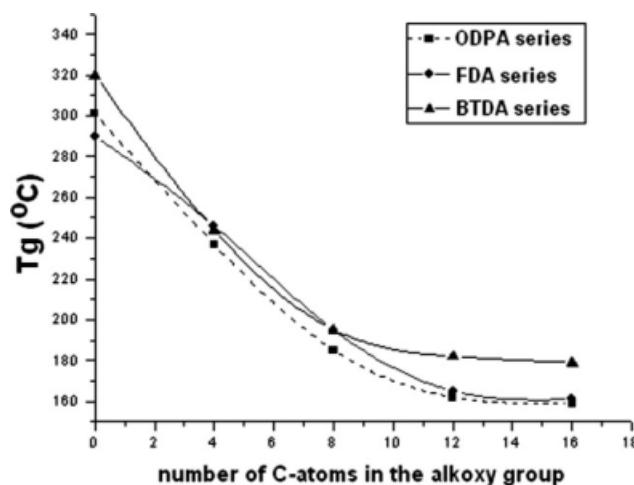


**Figure 7** Plot of $T_g$ values versus the number of carbon atoms in the alkoxy group of polyimides derived from 5-alkoxy-1,3-phenylenediisocyanates and aromatic dianhydrides.
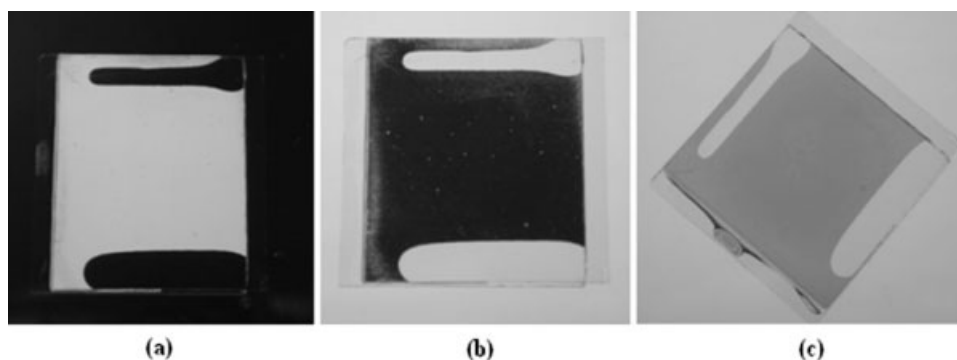
**Figure 8** Twisted nematic cell made from a polyimide derived from OPDC and ODPA (PI-2): (a) the cell between crossed polarizers, (b) the cell between parallel polarizers, and (c) the cell at 45° between crossed polarizers.

Further increases in the carbon chain length from 12 to 16 did not result in any further significant reduction in the $T_g$ values of the polyimides. As expected, the polyimides derived from flexible dianhydride, namely, ODPA, revealed the lowest $T_g$ values in the series of polyimides.

### Pretilt angle and electro-optical characteristics of the polyimide derived from OPDC and ODPA (PI-2)

The liquid-crystal cells were prepared as described in the Experimental section, and measurements were done by the crystal rotation method.[21] The pretilt angle was then calculated from the obtained incident angle.

Figure 8 shows photographs of the twisted nematic cell between the crossed and parallel polarizers made from the polyimide derived from 5-octyloxy-1,3-phenylenediisocyanate and ODPA (PI-2). Uniform alignment of the liquid crystals was observed. This opened the route for this polyimide to be used as an alignment layer for liquid-crystal displays. A pretilt angle of 2.97° was observed for PI-2, which is adequate for display applications. A low liquid-crystal pretilt angle is particularly attractive for in-plane-switching or twisted–nematic liquid-crystal display modes. Organosoluble polyimides are desirable, as their processing temperature is low; this feature is particularly important for low-temperature polysilicon thin-film transistor/liquid-crystal display processes.[7,8]

It has been reported that the polyimide main-chain structure greatly influences the liquid-crystal pretilt angle of alkyl-branched polyimide films. An asymmetric and flexible main-chain structure would lead to a small pretilt angle, whereas a symmetric and rigid main-chain structure would generate a high pretilt angle. One of the possible explanations for the low pretilt angle of the polyimide PI-2 was the presence of a flexible ether linkage in its
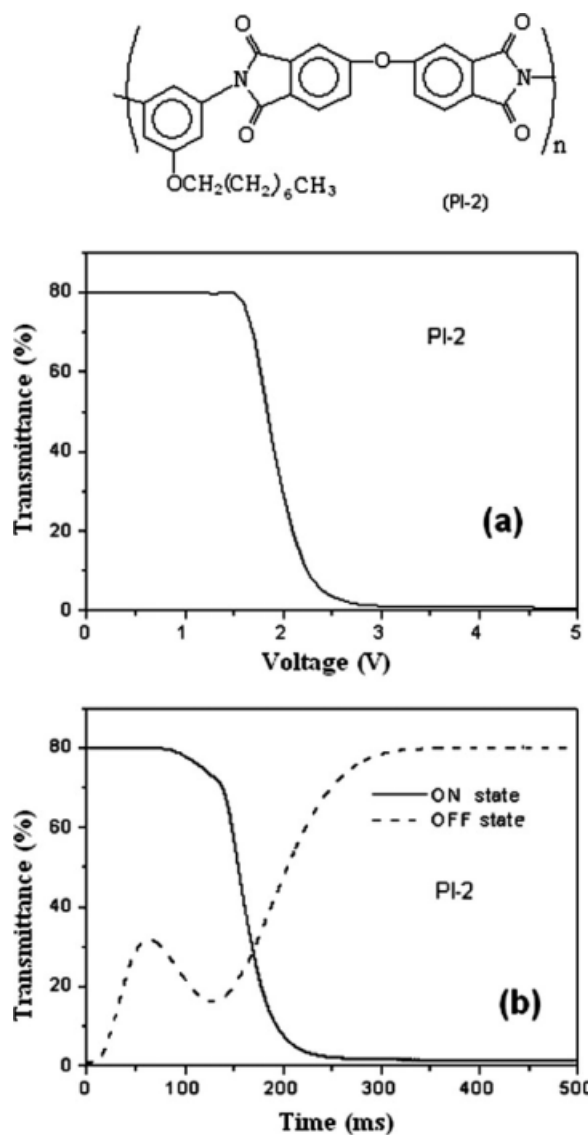


**Figure 9** (a) Electro-optical characteristics of a polyimide (PI-2) orientation layer and (b) response and relaxation times for a polyimide orientation layer from the nonselect state to the select state (5 V) at a frequency of 1000 Hz.

backbone and metacatenation. Further studies are necessary for definitive conclusions on what factors govern the pretilt angle.

Figure 9(a) shows a typical transmittance–voltage curve for normal incidence of the twisted nematic cell. A typical switching curve was observed with a switching voltage of nearly 3 V. The response and relaxation times of the twisted nematic cell are shown in Figure 9(b); a switching time of 65 ms was observed at 5 V. In the off state, because of the 18-µm cell thickness, a black flow effect was visible in the graph.

## CONCLUSIONS

Four new 5-alkoxy-1,3-phenylenediisocyanates, namely, BPDC, OPDC, DDPDC, and HDPDC, were synthesized from 5-alkoxyisophthalic acids by the Curtius rearrangement reaction and characterized by spectral methods. A series of polyimides was synthesized by the polycondensation of the 5-alkoxy-1,3-phenylenediisocyanates with commercially available aromatic dianhydrides in benzonitrile in the presence of DABCO as a catalyst. The inherent viscosities of the polyimides were in the range 0.16–0.43 dL/g. The polyimides obtained by the polycondensation of the 5-alkoxy-1,3-phenylenediisocyanates with FDA and ODPA were soluble in $m$-cresol, DCM, NMP, TCE, and pyridine and could be cast into transparent and flexible films from $m$-cresol or TCE. Wide-angle X-ray diffractograms revealed that layered structures were formed in the polyimides with longer pendent alkoxy chains. Polyimides containing a pendent alkoxy group had $T_g$ values that were significantly lower than those of the corresponding control polyimides without the pendent groups. The introduction of pendent alkoxy chains resulted in a decrease in the thermal stability of the polyimides. The polyimides displayed stepwise degradation behavior, which resulted from the degradation of the alkoxy side chain followed by the main chain. A pretilt angle of 2.97° was observed for the polyimide derived from OPDC and ODPA. This opens the route for this organosoluble polyimide to be used as an alignment layer for liquid-crystal devices.

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