Synthesis, Characterization, and Gas Permeability of Aromatic Polyimides Containing Pendant Phenoxy Group

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ABSTRACT: A diamine containing a pendant phenoxy group, 1-phenoxy-2,4-diaminobenzene, was synthesized and condensed with different aromatic dianhydrides [4,4'-oxydiphthalic dianhydride, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracorboxylic dianhydride, and pyromellitic dianhydride] by one-step synthesis at a high temperature in *m*-cresol to obtain polyimides in high yields. Most of the polyimides exhibited good solvent solubility and could be readily dissolved in chloroform, *sym*-tetrachloroethane, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and nitrobenzene. Their inherent viscosities were in the range of 0.33–1.16 dL/g. Wide-angle X-ray spectra revealed that these polymers were amorphous in nature. All these polyimides were thermally stable, having initial decomposition temperatures above 500°C and glass-transition temperatures in the range of 248–281°C. The gas permeability of 4,4'-oxydiphthalic dianhydride and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride based polyimides was investigated with pure gases: He, H_2, O_2, Ar, N_2, CH_4, and CO_2. A polyimide containing a $-C(CF_3)_2-$ linkage showed a good combination of permeability and selectivity. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3881–3889, 2008

Key words: gas permeation; membranes; polyimides; selectivity; structure-property relations

INTRODUCTION

Aromatic polyimides have wide applicability in electronics, coatings, high-modulus fibers, liquid-crystal displays, adhesives, and so forth because of their excellent thermal, electrical, and mechanical properties. Polyimides are being widely investigated as gas permeation[1–3] and pervaporation membrane materials[4] and as key materials in the electronics industry.[5] However, most of the polyimides have strong interchain attractive forces, dense molecular packing, and chain rigidity resulting in difficulty for processing and have poor solubility in organic solvents. Intensive efforts have been made to improve the processability of aromatic polyimides without affecting their characteristic properties. This has led to changes in the synthesis technique, such as making a poly(amic acid) precursor first, which has high solvent solubility, and then processing it in a poly(amic acid) stage.[6] However, this approach has certain limitations. Synthesizing a polyimide by thermal imidization of poly(amic acid) at a higher temperature, at which hazardous steps of cyclodehydration and re-

moval of nonvolatile polar solvents are unavoidable, causes voids, dimensional changes, crosslinking, low tractability, incomplete imidization, and stress formation.[7–9] Incessant efforts have been devoted to the synthesis of novel soluble and melt-processable fully imidized polyimides. This can be accomplished by a one-step solution imidization technique in which a stoichiometric mixture of monomers is heated in a high-boiling solvent in a temperature range of 140–250°C, within which the imidization reaction proceeds rapidly. Thermoplastic polyimides are preferentially made by solution imdization.[10] Structural modifications such as the introduction of bulky substituents,[11,12] aryl,[8] heterocyclic rings,[13] and flexible linkages[14] make aromatic polyimides more soluble.

Polyimide-based membranes are extensively being investigated for gas-permeation properties because of their high intrinsic selectivity,[1–3] especially for gas pairs involving CO_2.[15] The strategies used to develop processable aromatic polyimides for gas-separation applications include structural variations that lead to less molecular order and torsional mobility and lower intermolecular bonding.[16,17] The $-C(CF_3)_2-$ linkage in a polyimide hinders the rotation of the ring attached to it and lowers interchain interactions, leading to more free volume[18] and thereby conferring appreciable permeability and selectivity. The

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presence of the —C(CF$_3$)$_2$— linkage in a dianhydride moiety is more effective than in a diamine as the charge-transfer complex (CTC) formation declines sharply.[19] Furthermore, it has been reported that meta-substituted polyimides lead to a decrease in permeability and an increase in selectivity.[19,20]

In an effort to obtain processable and high-performance polymers, we decided to synthesize polyimides based on monomers containing a noncoplanar and bulky pendant phenoxy ring. The presence of this group in meta-linked polyimides was expected to provide molecular irregularity and good solubility. Moreover, the pendant phenoxy group in the side chain of polyimides offers sites for modification by substitution reactions to introduce functional groups such as sulfonic acid to alter the properties of polyimides for specific applications. This article describes the synthesis, characterization, and condensation polymerization of 1-phenoxy-2,4-diaminobenzene (PDAB) with different dianhydrides to obtain polyimides containing pendant phenoxy groups. The gas-permeability investigation of selected polyimides was performed to assess the effects of the pendant phenoxy group present on these polyimides.

EXPERIMENTAL

Materials

4,4′-Oxydiphthalic dianhydride (ODPA), 3,3′,4,4′-biphenyltetracorboxylic dianhydride (BPDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), pyromellitic dianhydride (PMDA), and 4,4′-oxydianiline (ODA) were purchased from Aldrich Chemicals (St. Louis, MO) and were purified by sublimation before use. Phenol, 1-chloro-2,4-dinitrobenzene, m-cresol, triethylamine, and all other solvents (analytical-reagent grade) were procured from S.D. Fine Chemicals (Mumbai, India) and used without further purification.

Synthesis of the monomer

1-Phenoxy-2,4-dinitrobenzene (PDNB)

A 250-mL, single-necked, round-bottom flask equipped with a condenser and a guard tube was charged with 9.411 g (0.1 mol) of phenol, 10.1 g (0.1 mol) of triethyl amine, 20.25 g (0.1 mol) of 1-chloro-2,4-dinitrobenzene, and 150 mL of acetone. The mixture was heated in an oil bath for 48 h at the reflux temperature of acetone. The solvent was then distilled off, and the residue was dissolved in chloroform (CHCl$_3$). This solution was washed with 5% HCl, 2% aqueous NaOH, and then water. The solution was dried over anhydrous Na$_2$SO$_4$ and filtered, and the

solvent was removed to obtain the crude product. It was recrystallized from methanol to obtain pale yellow crystals of PDNB. The spectral analysis was as follows.

Yield: 24.1 g (90%). mp: 75°C. ^{1}H-NMR (CDCl$_3$, ppm): 8.82 (d, 1H, J = 2.8 Hz, H_a), 8.35 (dd, 1H, J = 9.3, 2.8 Hz, H_b), 7.5 (t, 2H, J = 7.0 Hz, H_e), 7.35 (t, 1H, J = 7.4 Hz, H_f), 7.15 (d, 2H, J = 8.3 Hz, H_c), 7.05 (d, 1H, J = 9.4 Hz, H_d). Fourier transform infrared (FTIR; KBr, cm^{-1}): 1616, 1579 (aromatic), 1532 and 1346 (asymmetric and symmetric —NO$_2$ stretching), 1210 and 1070 (C—O—C asymmetric and symmetric stretching vibrations), and 875 cm^{-1} (C—N stretching). ANAL. calcd for PDNB (C$_{12}$H$_8$O$_5$N$_2$): C, 55.4%; H, 3.1%; N, 10.8%. Found: C, 55.5%; H, 3.1%; N, 10.6%.

PDAB

A Parr reactor was charged with 10 g (0.03846 mol) of PDNB, 70 mL of methanol, and 0.3 g of 5% Pd/C. It was heated at 65°C under 700 psi of hydrogen pressure for 4.5 h. When the absorption of hydrogen was complete, the contents were cooled and discharged after the pressure was released. The solution was then filtered to remove the catalyst and treated with activated charcoal. The product obtained after the removal of the solvent was recrystallized from methanol at a low temperature.

Yield: 6.7 g (87%). mp: 61°C. ^{1}H-NMR (CDCl$_3$, ppm): 7.35 (t, 2H, J = 8.0 Hz, H_e), 7.0 (t, 1H, J = 7.4 Hz, H_f), 6.9 (d, 2H, J = 7.7 Hz, H_d), 6.75 (d, 1H, J = 8.3 Hz, H_c), 6.1 (d, 1H, J = 2.5 Hz, H_a), 6.05 (dd, 1H, J = 8.3, 2.65 Hz, H_b), 3.35 (s, 4H, —NH$_2$). FTIR (KBr, cm^{-1}): 3358 and 3293 (asymmetric and symmetric N—H stretching, respectively), 1604 (N—H deformation), 1275 (C—N stretching), 1218 (C—O—C stretching). ANAL. calcd for PDAB (C$_{12}$H$_{12}$ON$_2$): C, 72.0%; H, 6.0%; N, 14.0%. Found: C, 72.0%; H, 6.4%; N, 14.0%.

Polymer synthesis

To a 50-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, N$_2$ gas inlet, and guard tube were added 2 g (0.010 mol) of PDAB and 8 mL of m-cresol. This solution was stirred for 15 min under a stream of N$_2$ at room temperature to dissolve the diamine. To this solution, an equimolar quantity of dianhydride and subsequently 10 mL of m-cresol were added at the ambient temperature under an N$_2$ atmosphere. Then, the temperature of the polymerization reaction was raised gradually to 200°C from the ambient temperature, and the reaction was heated at this temperature for 12 h. The water that formed during imidization was removed continuously with a stream of N$_2$. The resulting vis-

cous solution was then cooled and poured into 300 mL of methanol to precipitate the polymer. The polymer was washed several times with methanol and then dried at 100°C for 1 day in a vacuum oven. After drying, the polymer was dissolved in the appropriate solvent, reprecipitated in methanol, and finally dried at 60°C in a vacuum oven for a week.

Copolymer synthesis

Copolymers of PDAB and ODA with ODPA containing 5, 25, or 50 mol % PDAB were synthesized with a procedure similar to that described previously.

Preparation of the dense membranes

The dense membranes were prepared through the casting of a 2% *sym*-tetrachloroethane (TCE) solution of a polyimide based on PDAB with ODPA (PI-I) at 60°C onto a flat glass surface under a dry atmosphere, whereas in the case of a polyimide based on PDAB with 6FDA (PI-II), the solvent used was $CHCl_3$, and casting was performed at 40°C. After initial evaporation of the solvent, the formed film was peeled off and dried in a vacuum oven at 60°C for a week to remove the residual solvent. The complete removal of the solvent was confirmed by differential scanning calorimetry (DSC).

Measurements

The IR spectra were recorded on a PerkinElmer (Waltham, MA) 16 PC FTIR spectrophotometer. The ^{1}H-NMR spectra were recorded on a Bruker (Fallanden, Switzerland) AC-200. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA-7 in an N_2 atmosphere at a heating rate of 10°C/min. The glass-transition temperature (T_g) of the polyimides was measured with a DSC Q-10 (TA Instruments, New Castle, DE). The inherent viscosity of the polymers was determined at a 0.5 g/dL concentration at 35°C with an Ubbelohde viscometer. Elemental analysis was performed on an Elementar Vario-EL (Hanau, Germany).

The wide-angle X-ray diffraction (WAXD) spectra were obtained with a Rigaku Dmax 2500 diffractometer (Tokyo, Japan) with a Cu Kα radiation source. The amorphous peak maximum on each X-ray scattering profile was ascribed to the average intersegmental distance of polymer chains, and the *d*-spacing was calculated by substitution of the scattering value (2θ) of the peak into Bragg's equation, $n\lambda = 2d \sin \theta$, where $n = 1$ and λ is 1.54 Å for Cu Kα radiation. The density of the polyimides in film form was obtained by a floatation method with an aqueous K_2CO_3 solution (accuracy: ±0.001 g/cm^3). The fractional free volume (FFV) for PI-I and PI-II was determined as follows:

$$\text{FFV} = \left(\frac{V_{sp} - V_o}{V_{sp}} \right)$$

where V_{sp} is the specific free volume calculated from the molecular weight and density of the corresponding polyimide and V_o is the occupied volume. V_o is calculated from the correlation $V_o = 1.3V_w$, where V_w is the van der Waals volume calculated by Bondi's group contribution method.[21]

Gas-permeability evaluations

The pure gas-permeability coefficients for various gases (He, H_2, Ar, N_2, O_2, CH_4, and CO_2) were measured under isothermal conditions at 35 ± 0.1°C and at an upstream pressure of 10 atm with a standard technique based on a variable-volume method. All gases had a purity greater than 99.9%. Measurements were repeated with three different coupons cast under identical conditions, and the results were averaged as shown later in Table III. The variation in the permeation measurements for different gases was up to 15%.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The diamine PDAB was synthesized in two steps as described in the Experimental section (Fig. 1). Compound PDNB was obtained in good yields by a simple and convenient condensation reaction between 1-chloro-2,4-dinitrobenzene and phenol in acetone with triethylamine as an acid acceptor. PDNB was subsequently reduced in a Parr reactor with H_2 with 5% Pd/C as the catalyst to obtain PDAB in a high yield (87%).

The structures of diamine monomer PDAB and intermediate dinitro compound PDNB were confirmed by elemental analysis, IR, and ^{1}H-NMR. The IR spectra of monomer and polymers are shown in Figure 2 and Figure 3 respectively. The IR spectrum of PDNB showed absorption bands at 1532 and 1346 cm^{-1} due to asymmetric and symmetric —NO_2 stretching vibrations, respectively, whereas bands at 1210 and 1070 cm^{-1} were due to C—O—C asymmetric and symmetric stretching, respectively. A band at 875 cm^{-1} corresponded to an aromatic C—N stretching vibration. The ^{1}H-NMR spectrum also confirmed the structure of the dinitro compound; peaks in the region of δ = 7.0–9.0 showed the expected multiplet and integration, as shown in Figure 4(a).

The IR spectrum of PDAB showed bands at 3358 and 3293 cm^{-1} due to asymmetric and symmetric N—H stretching, respectively. The band at 1489 cm^{-1} corresponded to carbon–carbon stretching of the aromatic ring. A band at 1218 cm^{-1} was due to the ether linkage, and the band at 1275 cm^{-1} showed the C—N stretching. The structure of diamine

A] Monomer synthesis:

B] Synthesis of Homopolymer using PDAB:

C] Synthesis of Copolymer:

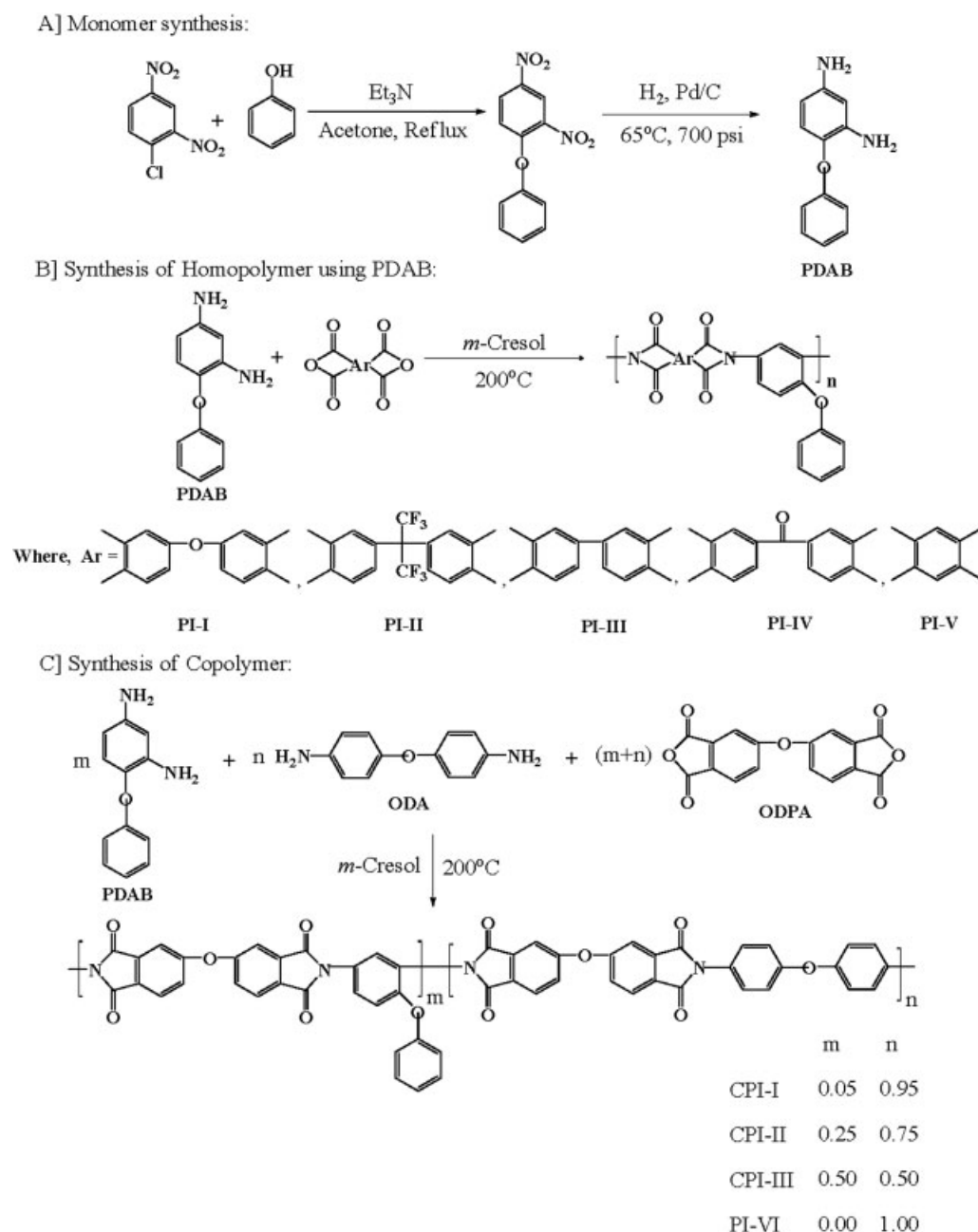|	m	n
CPI-I	0.05	0.95
CPI-II	0.25	0.75
CPI-III	0.50	0.50
PI-VI	0.00	1.00

Figure 1 Synthetic route to the monomer and polymers.

was further confirmed by the disappearance of the bands at 1532 and 1346 cm^{-1} due to asymmetric and symmetric stretching vibrations of the —NO$_2$ group of the starting nitro compound. The ^{1}H-NMR spectrum of diamine showed bands at $\delta = 3.0–3.5$ corresponding to —NH$_2$ protons. Aromatic protons in the region of $\delta = 6.0–7.5$ showed the expected multiplicity and integration values, as shown in Figure 4(b).

Polymerization and characterization

New polyimides containing pendant phenoxy groups were prepared from PDAB and aromatic dian-

hydrides such as ODPA, BTDA, BPDA, 6FDA, and PMDA by one-step high-temperature solution polymerization in m-cresol, as described in the Experimental section. All the reactions proceeded homogeneously without gelation or precipitation, except for the PMDA-based polyimide; in that case, the polymer precipitated from the solution. The polymers in solid form were obtained by the resultant viscous polymer solution being poured into methanol with vigorous stirring. The copolyimides of PDAB and ODA with ODPA containing 5, 25, and 50 mol % PDAB were synthesized with a similar procedure. The obtained polymers were characterized by FTIR
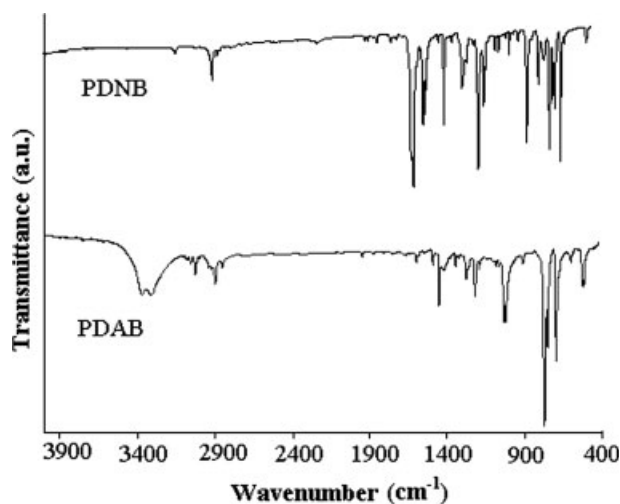
Figure 2 IR spectra of the monomer and its precursor.

Figure 4 NMR spectra of (a) precursor and (b) monomer (CDCl$_3$).

spectroscopy, WAXD, viscosity measurements, and thermal analysis. The physical properties of the investigated polyimides are given in Table I.

In the IR spectra of the polyimides, the characteristic absorption bands of the five-membered imide ring appeared at 1785 cm^{-1}, corresponding to asymmetric C=O stretching, at 1720 cm^{-1}, corresponding to symmetric stretching, at 1350 cm^{-1}, corresponding to C—N stretching, and at 1100 and 720 cm^{-1}, corresponding to imide ring deformation. A band at 1240 cm^{-1} was due to the ether group of the diamine. The complete imidization of the polymers was con-
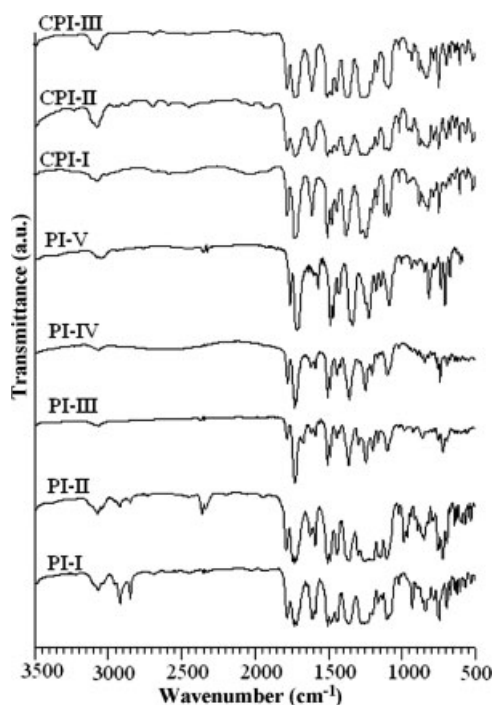
firmed by the absence of peaks at 1650, 1534, 1712 (acid C=O), and 3250 cm^{-1} (N—H and O—H groups) of amic acid.

Solubility and solution viscosity

The solubility of the polyimides and copolyimides was determined at a 0.5% concentration in a variety of organic solvents at the ambient temperature, as shown in Table II. Polyimides based on 6FDA and ODPA were soluble in many solvents, including chlorinated solvents. The high solubility of the 6FDA-based polyimides was attributed to the presence of the —C(CF$_3$)$_2$— linkage, which is known to increase the free volume in addition to decreasing the intermolecular interaction between the polymer chains.[18] Similarly, polyimides prepared from the ODPA dianhydride showed good solubility in polar aprotic solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), nitrobenzene, m-cresol, and chlorinated solvents. Polyimides based on BTDA (PI-III) and BPDA (PI-IV) were soluble at the ambient temperature only in m-cresol and on heating in polar aprotic solvents such as DMF, DMAc, and nitroben-

Figure 3 IR spectra of the polyimides and copolyimides.

TABLE I
Physical Properties of the Polyimides

Polymer	Diamine	Dianhydride	Inherent viscosity (dL/g)	T_g (°C)	IDT (°C)	T_{10} (°C)	Char yield (%)
PI-I	PDAB	ODPA	0.47[a]	256	580	608	59.02
PI-II	PDAB	6-FDA	0.43[a]	281	537	551	52.15
PI-III	PDAB	BTDA	0.34[a]	264	553	584	59.76
PI-IV	PDAB	BPDA	0.32[a]	248	555	594	58.65
PI-V	PDAB	PMDA	—	250	543	564	56.46
PI-VI	ODA	ODPA	1.91[b]	269	576	618	55.00
CPI-I	5% PDAB + 95% ODA	ODPA	0.38[c]	259	571	627	53.41
CPI-II	25% PDAB + 75% ODA	ODPA	1.16[a]	272	606	622	56.14
CPI-III	50% PDAB + 50% ODA	ODPA	0.57[a]	273	590	633	57.60

[a] 0.5 g/dL in DMAc at 35°C.
[b] 0.5 g/dL in m-cresol at 35°C.
[c] 0.5 g/dL in TCE at 35°C.
T_{10}, decomposition temperature at 10% weight loss.

zene because of their rigid structure. The polyimide based on PMDA (PI-V) was soluble in DMF and m-cresol only on heating, whereas the polyimide based on ODA and ODPA (PI-VI) was insoluble in any solvent except m-cresol, and that was also on heating. Thus, the solubility of ODA- and ODPA-based polyimides could be enhanced by the incorporation of PDAB as evidenced by the good solubility of the copolyimides in many solvents. These copolyimides were soluble even in TCE at the ambient temperature. The presence of the pendant phenoxy group on asymmetrically (meta) linked PDAB could also be responsible for the better solubility observed for these polyimides. The pendant phenoxy group with a flexible ether linkage could disrupt the chain packing in the polymer backbone to ease solvent solubility.

The inherent viscosity of the polyimides and copolyimides was determined with an Ubbelohde viscometer with a 0.5 g/dL solution concentration at 35°C. DMF was used as the solvent for the determination of the inherent viscosity as most of the polymers were soluble in it. The inherent viscosities of PI-I, PI-II, PI-III, PI-IV, CPI-II, and CPI-III were

measured in DMF, whereas the viscosities of PI-VI and CPI-I were determined in m-cresol and TCE, respectively, as they were not soluble in DMF. The viscosities of the polyimides based on PDAB ranged from 0.33 to 0.48 dL/g for homopolyimides and from 0.38 to 1.16 dL/g for copolyimides (Table I). The ODA (structural isomer of PDAB) -based polyimide showed higher viscosity than the PDAB-based polyimide obtained from the same dianhydride (ODPA). The comparatively low viscosity observed for the homopolyimides based on PDAB can be attributed to the steric hindrance created by ortho substitution of the phenoxy group to one of the —NH$_2$ groups in PDAB.

Thermal properties of the polymers

The thermal properties of all the polyimides and copolyimides, as evaluated by DSC and TGA, are summarized in Table I. The DSC and TGA spectra of these polyimides are shown in Figures 5 and 6, respectively. All polyimides and copolyimides had a high T_g value (>248°C). The increase in T_g generally

TABLE II
Solubility of the Polyimides and Copolyimides

Polymer	Solvent								
	CHCl$_3$	DMF	DMSO	NMP	Nitro-Bz	m-Cresol	DMAc	THF	TCE
PI-I	++	++	−	++	++	++	++	−	++
PI-II	++	++	−	++	++	++	++	−	++
PI-III	−	+	−	±	+	++	+	−	−
PI-IV	−	+	−	+	+	++	+	−	−
PI-V	−	+	−	−	−	+	−	−	−
PI-VI	−	−	−	−	−	+	−	−	−
CPI-I	−	−	−	−	−	+	−	−	++
CPI-II	+	+	−	±	−	+	+	−	++
CPI-III	+	+	−	+	+	+	+	−	++

+ = soluble on heating at 80°C; ++ = soluble at room temperature; ± = partially soluble; − = insoluble; DMSO = dimethyl sulfoxide; Nitro-Bz = nitrobenzene; THF = tetrahydrofuran.
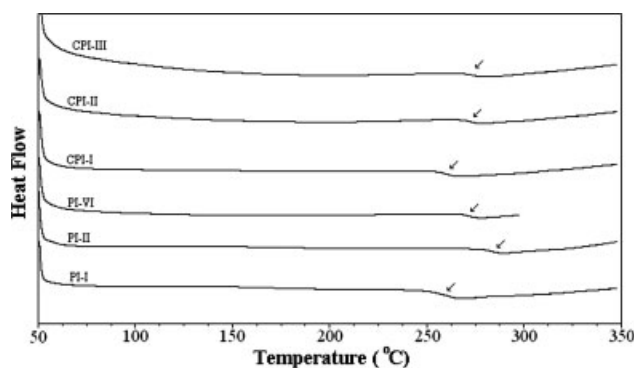
Figure 5 DSC of the polyimides and copolyimides.

corresponded to an increase in the rigidity of the dianhydride monomer. It is evident that the bridging group (—O—, —C=O) between the two phenyl rings present in dianhydrides such as ODPA and BTDA, facilitating bond rotation, reduced T_g. Among all the synthesized polyimides, PI-II based on 6FDA showed the highest T_g value because of the polarizable hexafluoroisopropylidene group, which inhibited the molecular motions. It has also been reported that the —C(CF$_3$)$_2$— linkage restricts the segmental mobility.[18] The T_g values of copolyimides synthesized by the addition of ODA to PDAB were marginally higher than T_g of the PDAB homopolymer. Although the incorporation of PDAB increased the free volume with a lowering of interchain interactions (as evidenced by increased solubility), the effect was counteracted by the decrease in the flexible linkage (C—O—C) present in ODA in the main chain.

The TGA curves of the polyimides and copolyimides are shown in Figure 6. Initially, the polymer samples were heated up to 220°C at a rate of 20°C/min in an N$_2$ atmosphere in a thermal analyzer to ensure the complete removal of the moisture/sol-
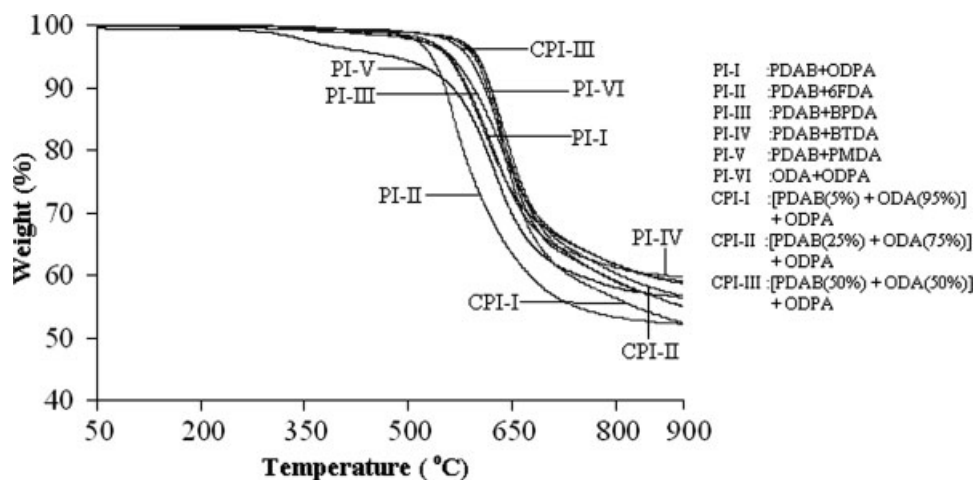
vent, if any, and then the samples were again weighed at 50°C and scanned further at a temperature rate of 10°C/min. All synthesized polyimides showed an initial decomposition temperature (IDT) above 500°C, thus exhibiting high thermal stability. However, among all the polyimides, IDT of PI-II was the lowest, despite the high C—F bond strength (441 kJ/mol).[21] It is known that the voluminous size of CF$_3$ retards the free rotation around its own axis, resulting in high torsional strain as well as a gain in high conformational energy.[22] It leads to the low thermal stability of the CF$_3$ group,[23] which is lost in the form of a CF$_3$ radical.[24] Because of the strong electron affinity of the F atom, the C—C bond energy in CF$_3$—C—CF$_3$ becomes lower.[25] Hence, a polymer with a —C(CF$_3$)$_2$— linkage demonstrated low thermal stability, which was exhibited by the lowest weight residue of the 6FDA-based polyimide in the series. All polyimides showed a char yield greater than 50%.

WAXD patterns revealed the complete amorphous nature of the synthesized polyimides. This observation was reasonable because the presence of the noncoplanar conformation of the 1-phenoxy-2,4-diamine decreased the intermolecular forces between polymer chains. The high d-spacing value of PI-II was due to the bulky nature of the fluorine atom in the —C(CF$_3$)$_2$—, and so the presence of the CF$_3$ group increased the free volume of the polymer chain, and this was accountable for its high density also.[21]

Gas permeability and permselectivity

To investigate the effect of the side-chain phenoxy group substituted at the 4-position of PDAB, the gas-permeation properties of two polyimides of PDAB with ODPA and 6FDA were investigated at 35°C. Dense membranes of these polymers, 40–50 μm thick, were prepared by a solution-casting

Figure 6 TGA of the polyimides and copolyimides.

TABLE III
Gas Permeability, Selectivity, and Relevant Physical Properties of PI-I and PI-II

Property	Polymer	
	PI-I	PI-II
Gas permeability[a]		
He	6.9	58
H$_2$	6.1	53
O$_2$	0.3	5.8
Ar	0.12	1.96
N$_2$	0.045	1.44
CH$_4$	0.017	0.44
CO$_2$	1.26	16.8
Selectivity[b]		
He/N$_2$	164	41
He/CH$_4$	406	131
O$_2$/N$_2$	7	4.1
CO$_2$/N$_2$	30	12
CO$_2$/CH$_4$	74	37
Density (g/cm^3)	1.354	1.416
Average interchain distance (Å)	4.23	5.82
FFV[c]	0.1425	0.1728

[a] Expressed in barrers [1 barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg].
[b] Ratio of the pure gas permeability.
[c] Determined by Bondi's group contribution method.

method. Although both polymers PI-I and PI-II were soluble in CHCl$_3$, TCE was used for PI-I as a membrane of this polymer prepared in CHCl$_3$ had a wavy surface. The gas-permeation results are summarized in Table III. The permeability coefficient of the 6FDA-based polyimide was considerably higher than that of the ODPA-based polyimide for the gases studied. The FFV and d-spacing values of the 6FDA-based polyimide were higher than those of the ODPA-based polyimide, and this led to higher permeability. Such an increase in the permeability as a result of a lowering of the packing density is known for polyimides containing —C(CF$_3$)$_2$— groups.[18] The incorporation of this group restricts the intrasegmental mobility of polymer chains, resulting in increased chain stiffness, as evidenced by the higher T_g of the 6FDA-based polyimide (PI-II) in comparison with that of the ODPA-based polyimide (PI-I). If the permeability difference for various gases in PI-I and PI-II is considered, the permeability in PI-II containing 6FDA was higher for bigger molecules such as N$_2$ and CH$_4$ than for smaller molecules such as He and H$_2$ in comparison with the respective gas permeability in PI-I based on ODPA. This phenomenon can be attributed to the availability of the free volume for diffusion and the kinetic diameter of the penetrants.[1,18] The effect of the incorporation of the hexafluoroisopropylidene group in increasing the permeability coefficient was less significant for smaller gases such as He and H$_2$ than for larger gases such as N$_2$ and CH$_4$ because smaller gases could diffuse

easily through the interstitial spaces.[2] PI-I exhibited excellent selectivity for various gas pairs. The potential for the incorporation of a pendant phenoxy linkage into the polyimide was depicted by the O$_2$/N$_2$ selectivity of 7, high He-based selectivity combined with high He or H$_2$ permeability, and CO$_2$/CH$_4$ selectivity of 74. The observed high permeability of He and H$_2$ in PI-II (58 and 53 barrer, respectively), coupled with the appreciable selectivity of He/CH$_4$ (131) and CO$_2$/CH$_4$ (37) in PI-II, further supported the usefulness of phenoxy group substitution in improving permeation properties.

It could be worth comparing the permeation properties of the present polyimides with those reported in the literature that exhibit structural similarities. The permeability of PDAB-based polyimides in this case was higher than that of respective polyimides based on unsubstituted *meta*-phenylene diamine (*m*-PDA) with either ODPA[26] or 6FDA.[27] This can be attributed to the introduction of the pendant phenoxy linkage into these polyimides. This increase in permeability, however, was found to be lower than that obtained by the introduction of a methyl group at the same position.[26] This could be ascribed to the flat nature of the phenyl ring, which is known to reduce permeability and increase selectivity in other families of polymers such as polyarylate[28] in comparison with their methyl-substituted analogues. It is interesting to note that the presence of the flexible —O— linkage of the phenoxy group in PDAB did not adversely affect the selectivity performance in comparison with polyimides based on methyl-substituted *m*-PDA and the respective dianhydride. This type of substitution thus needs further attention in this respect.

CONCLUSIONS

A diamine containing a pendant phenoxy group, PDAB, and polyimides based on this diamine with PMDA, ODPA, 6FDA, BTDA, and BPDA were synthesized and characterized for physical and gas-permeation properties. These polyimides showed good solvent solubility in common organic solvents. The low viscosity of the homopolyimides could be attributed to the phenoxy group substitution at the ortho position of the diamine, which reduced the reactivity of one amino group because of steric hindrance. The thermal properties of all the polyimides were high, as evidenced by their high T_g (>248°C) and high IDT values (>500°C). PI-II showed high d-spacing, high density, and high T_g but low IDT. PI-I had lower permeability and higher selectivity than PI-II. The appreciable permeability, high selectivity, and good solubility of PI-I and PI-II show the potential of pendant phenoxy group substitution in poly-

imides in governing gas-permeation properties favorably, and this needs to be pursued further.

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