Synthesis and Characterization of End-Capped Polyimides and Their Gas Permeability Properties

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ABSTRACT: Polyimides (PIs) based on 3,3′,4,4′-oxydiphthalic anhydride (ODPA) and 4,4′-oxydianiline (ODA) end capped with two new monoamines and other four different monoamines have been synthesized with a view to study the effect of different functional groups at the end of polymer chain on solubility, gas permeability, and thermal properties. The new monoamines have been synthesized from 3-pentadecylphenol, obtained by hydrogenation of cardanol, a major constituent of cashew-nut shell liquid. Introduction of different functional groups at the end of polyimide (PI) based on ODPA and ODA, by end capping with different monoamines, alters oxygen and nitrogen gas permeability, solubility, and thermal properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 627–635, 2000

Key words: cardanol; monoamines; end-capped polyimides; gas permeability membranes

INTRODUCTION

End capping of the polymers is a well-known technique used for introducing reactive functional groups at the ends. The technique is also used to control molecular weight of polymers or to block reactive functional groups at the end of a polymer. End-capped polyimides (PIs) have been reported in the literature. Various reactive functional groups such as acetylene,[1] biphenylene,[2] 4-phenylethynylphthalic anhydride,[3] diaryl substituted acetylene,[4] anthracene,[5] and 4-aminophthalonitrile[6] have been introduced at the end of PI oligomers for effective curing systems. End capping can also modify some of the properties of polymers. Thus PI end capped with phthalic an-

hydride improves thermal crystallization stability.[7] Melt flowability and processability of polycarbonate (PC) has been improved by end capping PC with 4-butoxymethylphenol.[8]

The present work was undertaken to study the effect of different monoamines used for end capping 3′,3′,4,4′-oxydiphthalic anhydride (ODPA) and 4,4′-oxydianiline (ODA) based PIs, on their solubility, gas permeability, and thermal properties.

EXPERIMENTAL

Materials

Cardanol was purchased from m/s card-chem., Thane, India. Ethanol and methanol (S. D. Fine chemicals, India) were distilled twice before use. Dimethyl formamide (DMF; S. D. Fine chemicals, India) was purified by azeotropic removal of water

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with toluene and then distillation over calcium oxide (S. D. Fine chemicals, India) under nitrogen. Raney Nickel was prepared from a "nickel-aluminum" alloy (S. D. Fine chemicals, India) as per the procedure[9] for W_2 catalyst. Potassium carbonate (K_2CO_3; S. D. Fine chemicals, India) was powdered and dried well by heating at 100°C in vacuum oven for 12 h. ODPA and ODA (Aldrich, USA) were purified by vacuum sublimation. 4-Aminophenol, 1,2-dichloro-4-nitrobenzene, 1-chloro-4-nitrobenzene, and sulphanilic acid (all purchased from S. D. Fine chemicals, India) were used without further purification. All the other chemicals were reagent grade and used as received.

Measurements

Fourier transform infrared (IR) spectra were recorded on Perkin Elmer 16 PC spectrophotometer. [1]H-Nuclear Magnetic Resonance (NMR) spectra were recorded on 300 and 200 MHz Bruker NMR spectrophotometer at room temperature. Elemental analyses were carried out by CHNS-O, EA 1108-Elemental Analyzer of Carlo-Erba Bruker Instrument. Thermal analyses of polymers were carried out using a Perkin Elmer TGA-7 and DSC-7 instrument at a heating rate of 10°C/min, under nitrogen. Inherent viscosity measurements were made using a Ubbelhode viscometer with 0.5 g dL^{-1} solutions at 30.0 ± 0.1°C. X-ray analyses were carried on Rigaku Dmax 2500 X-ray diffractometer.

MONOMER SYNTHESIS

Synthesis of 3-Pentadecylphenol or Tetrahydroanacardol (THA)

Freshly distilled cardanol (90.0 g, 0.3 mol) was hydrogenated with Raney nickel catalyst (1.8 g, 2 wt % based on cardanol) at 70°C and 600 psi hydrogen pressure for 4 h in a Parr medium hydrogenator (300 mL capacity) provided with a variac to control the heat in put, a dial thermometer, a mechanical stirrer operating at 500 rpm and a pressure gauge. The catalyst was removed by filtration and 3-pentadecylphenol obtained was recrystallized from hexane. (Yield 76 g, 83%; mp, 49–50°C) (lit.[10] mp 51°C). IR (CHCl$_3$): ν = 3350, 1620, 1470 cm^{-1}; ^{1}H-NMR (CDCl$_3$, δ ppm): 0.86 (t, J = 8 Hz, 3H), 1.26 (br s, 24H), 1.50–1.70 (m, 2H), 2.54 (t, J = 8 Hz, 2H), 5.30 (br

s, 1H), 6.60–6.80 (m, 3H), 7.13 (t, J = 8 Hz, 1H); Anal. Calcd for C$_{21}$H$_{36}$O: C, 82.89; H, 11.84. Found: C, 82.83; H, 11.85.

Synthesis of 4-Amino-3-pentadecylphenol (THA-NH$_2$)

Into a 500 mL, three-necked, round-bottom flask equipped with a reflux condenser, thermowell, and an overhead stirrer were added 3-pentadecylphenol (30.4 g, 0.1 mol), potassium hydroxide (28 g, 0.5 mol), and 95% ethyl alcohol (200 mL). The mixture was stirred and the obtained solution was cooled to −5°C and to this was added diazonium chloride prepared from sulphanilic acid dihydrate (21.0 g, 0.1 mol). The resulting red dye solution was stirred for 2 h and then heated to 75°C on a water bath. At this temperature a saturated solution of sodium dithionite (53.0 g, 0.3 mol) was added to the dye solution in 10 min and was stirred for 30 min (color changed from dark red to orange). To this was added acetic acid (18 g, 0.3 mol) in water (20 mL) and refluxed for 1 h (color changed to pale tan). The reduced solution was then poured into water (2 L) and the product was filtered, dried under vacuum at 50°C for 2 h. The crude product obtained was purified by recrystallization using toluene. (Yield 25 g, 79%; mp, 104–106°C) (lit.[10] mp 105–106°C). IR (CHCl$_3$): ν = 3400, 3350, 1620, 1500 cm^{-1}; ^{1}H-NMR (DMSO-d$_6$, δ ppm): 0.86 (t, J = 8 Hz, 3H), 1.25 (br s, 24H), 1.36–1.56 (m, 2H), 2.29 (t, J = 8 Hz, 2H), 6.28–6.50 (m, 3H); Anal. Calcd for C$_{21}$H$_{37}$NO: C, 78.99; H, 11.59; N, 4.38. Found: C, 78.8; H, 11.56; N, 4.5.

Synthesis of 4-Amino-3′-pentadecyldiphenyl ether (THAMA)

Synthesis of 4-Nitro-3′-pentadecyldiphenyl ether (NPDE)

A 50-mL, three-necked, round-bottom flask equipped with magnetic stirrer, nitrogen gas inlet, and reflux condenser was charged with THA (3 g, 9.8 mmol), 1-chloro-4-nitrobenzene (1.55 g, 9.8 mmol), potassium carbonate (1.5 g, 10.9 mmol), and DMF (15 mL). The reaction mixture was refluxed for 3 h under dry nitrogen gas stream. It was then cooled to room temperature and poured in water to precipitate the product. The crude product was filtered, dried and recrystallized from ethanol. (Yield 3.79 g, 91%; mp 45–47°C). IR (CHCl$_3$): ν = 1620, 1580, 1520, 1500,

1470, 1350, 1260 cm^{-1}; ^{1}H-NMR (CDCl$_3$, δ ppm): 0.90 (t, J = 8 Hz, 3H), 1.26 (br s, 24H), 1.52–1.70 (m, 2H), 2.65 (t, J = 8 Hz, 2H), 6.85–7.40 (m, 6H), 8.23 (d, J = 8 Hz, 2H); Anal. Calcd for C$_{27}$H$_{39}$NO$_3$: C, 76.24; H, 9.18; N, 3.30. Found: C, 76.19; H, 9.20; N, 3.1.

Reduction of NPDE

NPDE (2 g, 5.0 mmol), 10% palladized charcoal (Pd/C) (0.02 g), and ethanol (15 mL) were introduced into a two-necked, 50-mL, round-bottom flask equipped with a reflux condenser and a thermowell. To the reaction mixture, hydrazine hydrate (5 mL) was added dropwise over a period of 0.5 h at 80°C. After the addition was complete, the reaction was continued at reflux temperature for another 5 h. The reaction mixture was then filtered to remove Pd/C. Crystals precipitated on cooling were isolated by filtration and recrystallized twice from ethanol. (Yield 1.78 g, 90%; mp, 63–65°C). IR (CHCl$_3$): ν = 3445, 3400, 1620, 1590, 1488, 1460, 1250, 1210, 1175 cm^{-1}; ^{1}H NMR (CDCl$_3$, δ ppm): 0.90 (t, J = 8 Hz, 3H), 1.26 (br s, 24H), 1.45–1.7 (m, 2H), 2.55 (t, J = 8 Hz, 2H), 4.7 (br s, 2H), 6.60–6.95 (m, 7H), 7.20 (t, J = 8 Hz, 1H); Anal. Calcd for C$_{27}$H$_{41}$NO: C, 82.03; H, 10.34; N, 3.55. Found: C, 82.00; H, 10.36; N, 3.51.

Synthesis of 4-Amino-2-chloro-3′-pentadecyldiphenyl ether (THA-MACl)

Synthesis of 4-Nitro-2-chloro-3′-pentadecyldiphenyl ether (THA-MNCl)

A 50-mL, three-necked, round-bottom flask equipped with magnetic stirrer, nitrogen gas inlet, and reflux condenser was charged with THA (3 g, 9.8 mmol), 1,2-dichloro-4-nitrobenzene (1.89 g, 9.8 mmol), potassium carbonate (1.5 g, 10.9 mmol), and DMF (15 mL) under nitrogen gas stream. The reaction mixture was refluxed for 3 h under dry nitrogen gas stream. The mixture was then cooled to room temperature and poured in water to precipitate the product. The crude product was filtered, dried, and recrystallized from ethanol. (Yield 4.14 g, 92%; mp, 53–55°C). IR (CHCl$_3$): ν = 1620, 1578, 1520, 1480, 1450, 1350, 1270, 1225 cm^{-1}; ^{1}H-NMR (CDCl$_3$, δ ppm): 0.90 (t, J = 8 Hz, 3H), 1.27 (br s, 24H), 1.50–1.71 (m, 2H), 2.65 (t, J = 8 Hz, 2H), 6.80–7.45 (m, 5H), 8.09 (dd, J = 3 & 8 Hz, 1H), 8.4 (d, J = 3 Hz, 1H); Anal. Calcd for C$_{27}$H$_{38}$ClNO$_3$: C, 70.51; H, 8.27;

N, 3.05; Cl, 7.73. Found: C, 70.49; H, 8.30; N, 3.00; Cl, 7.70.

Reduction of THA-MNCl

THA-MNCl (2 g, 4.7 mmol), 10% Pd/C (0.02 g), and ethanol (15 mL) were introduced into a two-necked, round-bottom flask equipped with a reflux condenser and a thermowell. To the reaction mixture, hydrazine hydrate (5 mL) was added dropwise over a period of 0.5 h at 80°C. After the addition was complete, the reaction was continued at reflux temperature for another 5 h. The mixture was then filtered to remove Pd/C. Crystals precipitated on cooling were isolated by filtration and recrystallized twice from ethanol. (Yield 1.84 g, 91%; mp 56–57°C). IR (CHCl$_3$): ν = 3500, 3380, 1620, 1595, 1490, 1463, 1250, 1210, 1200, 1175 cm^{-1}; ^{1}H-NMR (CDCl$_3$, δ ppm): 0.90 (t, J = 8 Hz, 3H), 1.26 (br s, 24H), 1.45–1.7 (m, 2H), 2.55 (t, J = 8 Hz, 2H), 4.60 (br s, 2H), 6.60–6.90 (m, 6H), 7.20 (t, J = 8 Hz, 1H); Anal. Calcd for C$_{27}$H$_{40}$ClNO: C, 75.44; H, 9.31; N, 3.26; Cl, 8.27. Found: C, 75.30; H, 9.27; N, 3.24; Cl, 8.24.

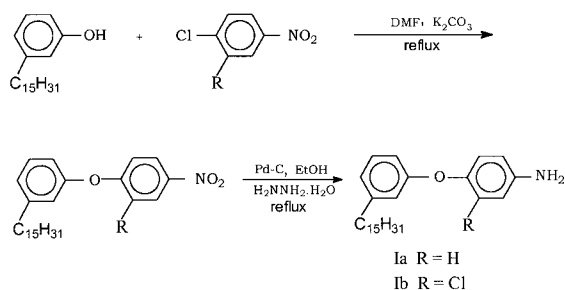### Synthesis of 4-Aminodiphenyl ether (PhOPhNH$_2$)

4-Aminodiphenyl ether was synthesized by condensing phenol and 1-chloro-4-nitrobenzene followed by reduction by the same procedure as described in under Synthesis of THAMA. Yield was 89% and melting point 82°C.

GENERAL PROCEDURE FOR SYNTHESIS OF POLYIMIDES

A 50 mL, three-necked, round-bottom flask equipped with an overhead stirrer, nitrogen gas inlet, and a guard tube was charged with ODPA : ODA : monoamine, in the mole ratio of 60 : 59 : 2,
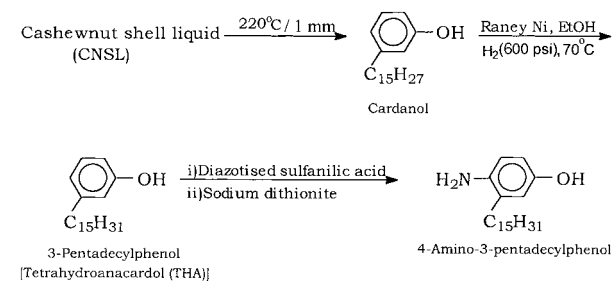
Scheme 1 Synthesis of 4-amino-3-pentadecylphenol.

Scheme 2 Synthesis of 4-amino-3′-pentadecyldiphenyl ether (THA-MA, Ia) and 2-chloro-4-amino-3′-pentadecyldiphenyl ether (THA-MACl, Ib).

respectively, (In the case of PIM-1, only ODPA : ODA was taken in the mole ratio 60 : 59), in *m*-cresol (15% solid content), and the solution was heated under the stream of nitrogen gas for 6–8 h in an oil bath, maintained at 200°C. After cooling, the viscous solution was poured slowly in methanol to precipitate the polymer. The polymer was washed four times with methanol and stirred overnight in methanol to remove *m*-cresol. The polymer after filtration was dried in a vacuum oven at 80°C for 12 h. Polymer yields were ∼ 98% in all cases. The polymers were analyzed by IR, NMR, viscosity, thermal gravimetric analyzer (TGA), and differential scanning calorimeter (DSC).

MEMBRANE PREPARATION

The polymer (0.1 g) was dissolved in a solvent combination of chloroform (2 mL) and *m*-cresol (2 drops). The clear solution was filtered (to remove any insoluble impurities) into a leveled petri dish of 5 cm inner diameter and kept in a controlled dust free chamber at ambient temperature for 24 h. A good transparent film was obtained. This film was heated under continuous high vacuum at 90°C for 8 h and kept in vacuum for 48 h. Thicknesses of the films were in the range of 0.055–0.056 mm.

RESULTS AND DISCUSSION

In order to study the effect of long alkyl groups and other substituents only at the end of PIs on their properties, PIs based on ODPA and ODA end capped with six different monoamines were synthesized in *m*-cresol, as described in the experimental part. For comparative studies, three monoamines containing an alkyl group and three monoamines without alkyl groups were used for end capping. Monoamine containing a long alkyl group and phenolic hydroxyl group (4-amino-3-pentadecylphenol) was synthesized[10] from 3-pentadecylphenol as shown in Scheme 1.

Two new monoamines, one (4-amino-3′-pentadecyldiphenyl ether) containing a long alkyl group and another (4-amino-2-chloro-3′-pentadecyldiphenyl ether) containing a long alkyl group, and a chloro substituent have been synthesized in good yields by condensing 3-pentadcylphenol with 1-chloro-4-nitrobenzene and 1,2-dichloro-4-nitrobenzene, respectively, followed by reduction using hydrazine hydrate and 10% Pd/C (Scheme 2). The
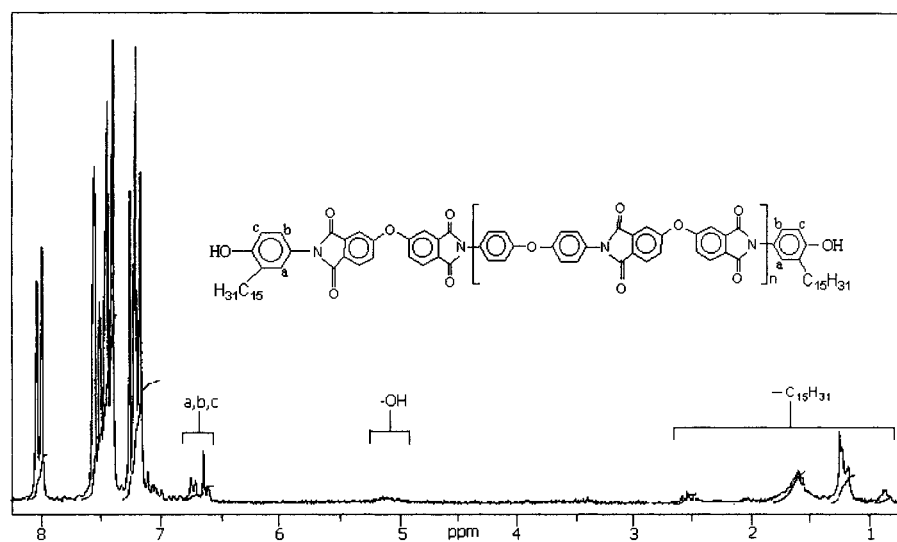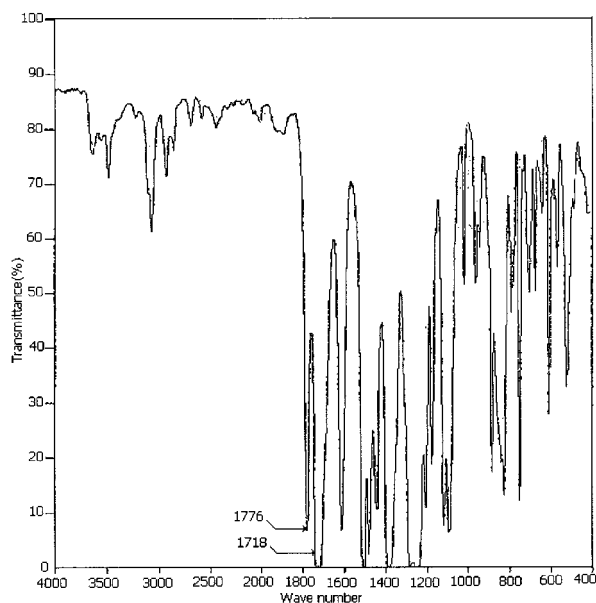

Figure 1 ¹H-NMR spectra of PIM-5.

Figure 2 IR spectra of PIM-5.

structures of these two new monoamines (Ia and Ib) were confirmed by IR, NMR, and elemental analysis.

Aniline, 4-aminophenol, and 4-aminodiphenyl ether (PhOPhNH$_2$) were used for end capping to synthesize PIs without an alkyl group at the ends for comparative studies.

A ratio of ODPA : ODA : monoamine, 60 : 59 : 2, was selected to obtain PIs with sufficiently high molecular weight of $\sim$ 30,000, so as to get a film of good physical properties. All PIs were obtained in high yield ($\sim$ 98%). Complete imidization of polymers was confirmed by the absence of peaks corresponding to —NH$_2$ and —COOH, in NMR and IR spectra. (For example, Figs. 1 and 2.)

The molecular weights of these PIs were determined by proton NMR, by comparing methyl protons of the long alkyl group with aromatic protons. The molecular weight obtained were $\sim$ 28,000, slightly lower than the targeted molecular weight.

Solubility Properties

Solubility behavior of these PIs in different solvents was studied by preparing 5% solution (Table I).

Polyimide of ODPA and ODA (1 : 1) was insoluble in all other solvents except m-cresol, whereas ODPA : ODA (60 : 59) is soluble in chloroform, NMP, DMAc, and m-cresol, and partly soluble in pyridine, nitrobenzene and DMF; it is insoluble in toluene.

End capping of this PI with aniline (PIM-2) and 4-aminophenol (PIM-3) slightly improves its solubility in pyridine and nitrobenzene (according to percent solubility), but its solubility in chloroform is reduced. Whereas end capping with 4-amino-3-pentadecylphenol (PIM-5) (Figs. 1 and 2), 4-amino-3′-pentadecyldiphenyl ether (PIM-6) (Fig. 3), and 4-amino-3-chloro-3′-pentadecyldiphenyl ether (PIM-7) (Fig. 3), which contain a long alkyl group enhances the solubility of these PIs in toluene (PIM-5 and 6), and in nitrobenzene (PIM-5, 6, and 7). Also the degree of solubility of PIM-5, 6, and 7 in chloroform is more than it is for PIM-1, but their solubility is reduced in DMAc. These results show that the structure of the monoamine used for end capping influences solubility characteristics of PIs.

Inherent viscosities of these PIs were determined in an Ubbelhode Viscometer at 30.0

Table I   Solubility Behavior of Polyimides[a]

Polymer	CHCl$_3$	m-cresol	NMP	DMF	DMAc	Pyridine	Toluene	Nitro-benzene
PIM-1	++	++	++	±	++	±	−	±
PIM-2	±	++	++	±	±	±	−	±
PIM-3	±	++	++	±	−	±	−	±
PIM-4	±	++	++	±	±	±	−	±
PIM-5	++	++	++	±	±	±	±	++
PIM-6	++	++	++	±	±	±	±	+
PIM-7	++	++	++	±	±	±	−	++

[a] ++: Soluble at room temp; +: soluble on heating; ±; partially soluble/swelling; −: insoluble. PIM-1: ODPA + ODA (60 : 59); PIM-2: ODPA + ODA + aniline (60 : 59 : 2); PIM-3: ODPA + ODA + 4-aminophenol (60 : 59 : 2); PIM-4: ODPA + ODA + PhOPhNH$_2$ (60 : 59 : 2); PIM-5: ODPA + ODA + THA-NH$_2$ (60 : 59 : 2); PIM-6: ODPA + ODA + THA-MA (60 : 59 : 2); PIM-7: ODPA + ODA + THA-MACl (60 : 59 : 2). [NMP: 1-Methyl-2-pyrrolidinone, DMAc: N,N-Dimethylacetamide].

PIM - 6   R = H
PIM - 7   R =Cl
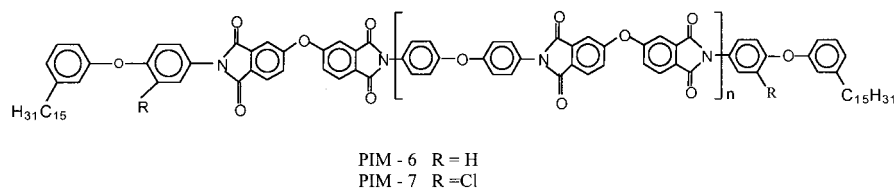
Figure 3   Polyimide chain end capped with new monoamines.

± 0.1°C, in chloroform or NMP depending on their solubility. All of the PIs have inherent viscosity above 0.6 dL g^{-1} (Table II) and they have sufficiently high molecular weight and form good transparent films.

Thermal Analysis

Thermal stability is an important property of polyimides. There has been a constant effort to improve processability without affecting thermal properties of PIs. It is well known that introduction of alkyl group in side chain of PI by using diamines containing an alkyl side chain reduces T_g significantly. However, the effect of the alkyl group only at the end on thermal properties of PI has not been studied yet.

In the present study thermal behavior of these polymers was evaluated by TGA and derivative of thermogravimetry by heating the polymer sample at a constant rate of 10°C/min in nitrogen (Table II). Representative thermograms are shown in Figures 4 and 5.

All the polyimides have similar decomposition pattern. End capping with aniline improves thermal stability marginally; no change was observed in T_g. However, introduction of phenolic hydroxyl group at the end decreases thermal properties. End capping with 4-aminophenol (PIM-3) and

3-pentadecyl-4-aminophenol (PIM-5) decreases initial decomposition temperature by ~ 27°C. Comparison of initial decomposition temperature (IDT) between PIM-4 and PIM-6 indicates that the IDT decreases slightly by incorporating alkyl side chain at the end of PI chain. Interestingly IDT of polyimide end capped with 4-amino-2-chloro-3′-pentadecyldiphenyl ether, which contains chlorine and alkyl group, increases significantly. Thermal stability of this polymer is slightly superior compared to other polyimides. T_g was determined using DSC (Fig. 6), by heating the sample in nitrogen at a constant rate of 10°C/ min. T_g of PIs vary between 240 and 261°C.

There is significant reduction in T_g of PIM-5, -6, and -7. This effect may be due to the alkyl group present on the end-capped monoamine (Table II). Thus introduction of the alkyl group at the end of polyimides does not affect thermal stability significantly, though it reduces the glass transition temperature. Thus these polyimides may be processed at a lower temperature without significant change in thermal stability of these polymers.

X-ray Diffraction of Polymers

Crystallinity of these polyimides was examined by wide-angle X-ray diffraction diagrams. The

Table II   Viscosity, TGA, and DSC Analysis of Polyimides[a]

| Polymer | Solvent Used for Viscosity | Inherent Viscosity (dL/g) | TGA (°C) | | | DSC, T_g (°C) |
			IDT	10% Decomposition	T_{max}	
PIM-1	CHCl$_3$	0.75	527	570	616	260
PIM-2	NMP	0.79	535	557	622	260
PIM-3	NMP	0.78	500	543	601	261
PIM-4	NMP	0.76	522	555	637	255
PIM-5	CHCl$_3$	0.66	500	528	608	250
PIM-6	CHCl$_3$	0.62	507	543	603	240
PIM-7	CHCl$_3$	0.61	560	574	606	241

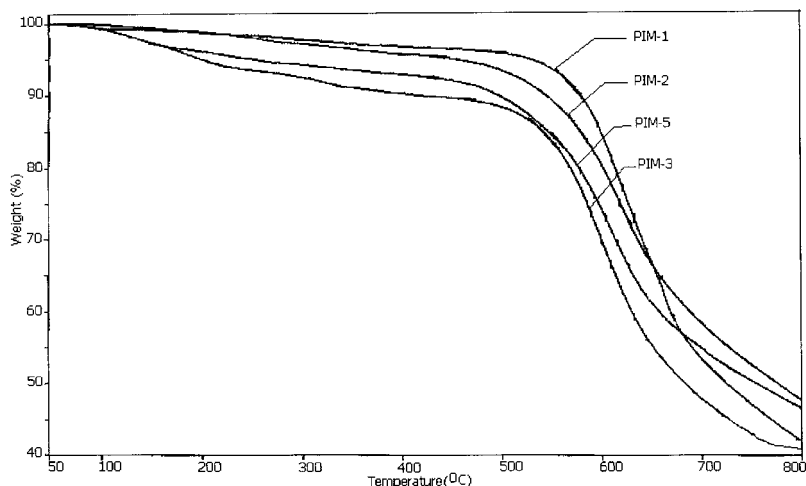[a] IDT: initial decomposition temperature; T_{max}: maximum decomposition temperature.

Figure 4 Thermogravimetric analysis of polyimides.

polyimide films obtained by solution casting were employed as samples. X-ray analysis indicates the absence of crystallinity in resulting polymers. All polymers were amorphous in nature (Fig. 7).

Gas Permeability

Large free volume, and excellent thermal and physical properties, have placed polyimides as a material of choice for gas transport. Polyimide membranes can be used at higher temperature. However, polyimides have low permeability for gases and structural variations to achieve higher permeability, and selectivity for gases is desired. Introduction of alkyl groups should increase gas permeability of polyimides. In order to study the effect of the long alkyl group at the end, on gas transport properties of polyimides, we determined oxygen and nitrogen gas permeability of end-capped polyimides.

Polymer membranes prepared by the procedure as given in the experimental section were used as samples to determine gas permeability. All the solvents and solvent mixtures listed in Table I were tried to prepare a transparent membrane with good strength, but only the chloroform and *m*-cresol solvent mixture formed good membranes.

Gas permeability of these polyimides for oxygen and nitrogen gas was studied at $30 \pm 0.1°C$ on
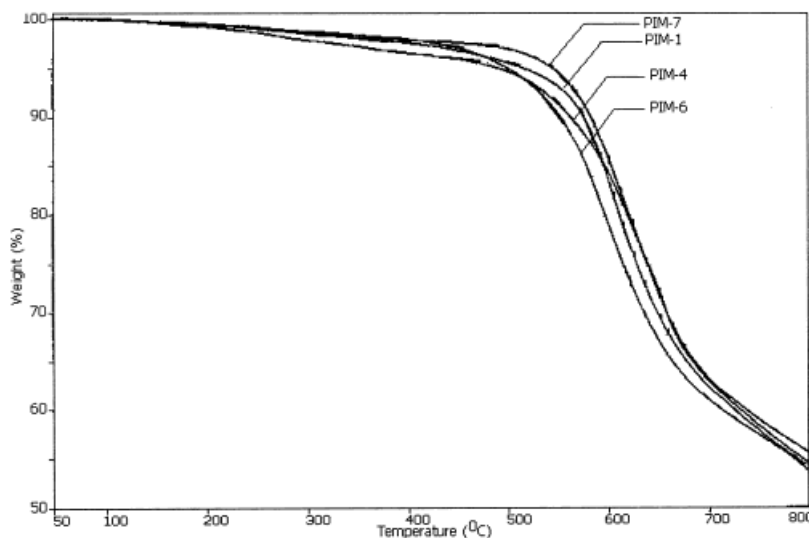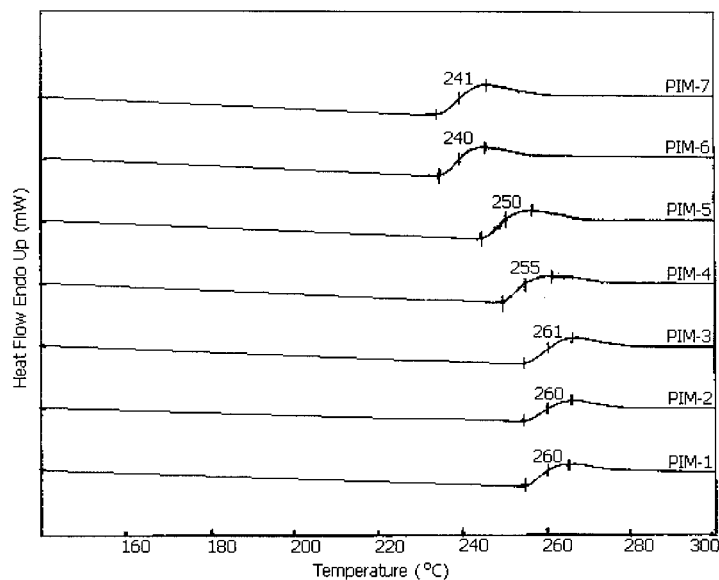

Figure 5 Thermogravimetric analysis of polyimides.

Figure 6   DSC thermograms of polyimides.

a permeability cell by measuring permeated gas by a capillary tube using a mercury slug under known gas pressure.[11] Reproducibility was checked for three films of the same polymer. The gas permeability was calculated by the following equation:

$$P = \frac{l}{(P_1 - P_2)} \times \frac{q/t}{A}$$

where P is the gas permeability [cm^3 (STP)/cm^2 s cm Hg], q/t is the volume flow rate of gas permeate [cm^3 (STP)/s], l is the thickness (cm) of membranes, and P_1 and P_2 are pressures (cm Hg) on the high pressure and low pressure side of the membrane, respectively. A is the effective membrane area (cm^2).

Unit: 1 barrer = 10^{-10} cm^3 (STP) cm/cm$^2 \cdot$ s $\cdot$ cm Hg

Permeability results for oxygen and nitrogen are tabulated in Table III. All polyimides have the same polymer backbone of ODPA and ODA, but differ in the structure of end-capped monoamines.

Polyimide based on ODPA and ODA (PIM-1) without end capping has low permeability of 0.046 barrer for nitrogen and 0.18 barrer for oxygen and permselectivity for O$_2$/N$_2$ ~ 4.0. End capping of this polymer with 4-aminodiphenyl
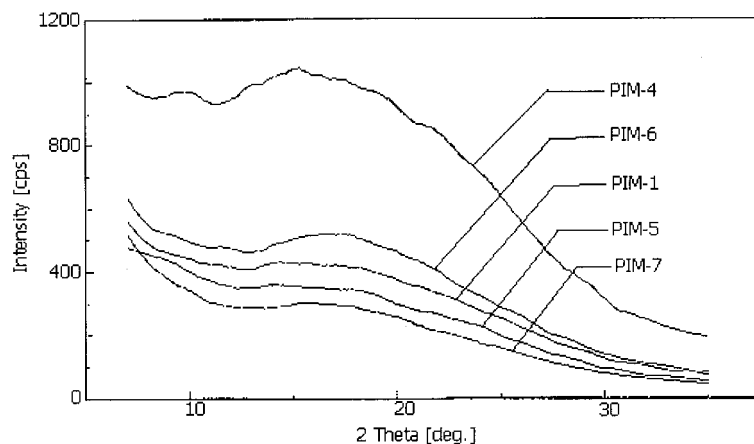
Figure 7   X-ray patterns of polyimides.

Table III   Permeability and Selectivity Data of Different Polyimides

Polymer	P_{N_2} Barrer	P_{O_2} Barrer	$\alpha = P_{O_2}/P_{N_2}$
PIM-1	0.046	0.18	3.93
PIM-4	0.062	0.17	2.8
PIM-5	0.11	0.28	2.35
PIM-6	0.09	0.32	3.55
PIM-7	0.045	0.26	5.7

[a] P_{O_2}: oxygen permeability; P_{N_2}: nitrogen permeability; ($\alpha = P_{O_2}/P_{N_2}$): selectivity.

ether (PIM-4) does not change oxygen permeability, though there is slight increase in nitrogen permeability. Introduction of the alkyl group at the end (PIM-5 and PIM-6) increases both nitrogen and oxygen gas permeability, though there is slight reduction in permselectivity. Introduction of chlorine and the alkyl group at the end (PIM-7) increases oxygen permeability without any change in nitrogen permeability, thus improving its permselectivity. These results indicate that the structure of the end group influences the gas permeability properties of the polyimides investigated.

Though in the present studies the difference in properties due to end capping is not very large, it is significant to indicate that end groups influence properties of polyimides, and by introducing a bulky group with many alkyl long chains or an oligomer containing bulky groups and other functional groups at the end of polyimides should influence solubility as well as thermal and gas transport properties of polyimides. Further, it may be possible to monitor gas transport properties of polyimides by monitoring the structure of capped ends.

CONCLUSIONS

The present work describes the synthesis of two new monoamines, starting from cashew-nut shell liquid. End capping of ODPA- and ODA-based polyimide with six different monoamines including two new monoamines shows variation in solubility properties of these polyimides in different organic solvents. Also, the glass transition temperature was reduced in the case of polyimides end capped with monoamines containing an alkyl C_{15} side chain, without much effect on thermal stability. Significant, though not very large differences, were observed in nitrogen and oxygen gas permeability by changing the end groups.

Thus the structure of monoamine end-cap influences solubility, and thermal and gas permeability properties of ODPA- and ODA-based polyimides.

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