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Synthesis and characterization of polyimides containing naphthalene pendant group and flexible ether linkages

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Abstract

A series of novel polyimides containing naphthalene pendant moieties were prepared from various diamines (including bis(4-amino-3,5-dimethylphenyl)naphthylmethane **1**, bis(4-aminophenoxy-3,5-dimethylphenyl)naphthylmethane **4**, and bis(4-aminophenoxy-3,5-dimethylphenyl)methane **5**) with various aromatic tetracarboxylic dianhydrides via both two-step and one-step methods. All polyimides, except $\mathbf{8}_{\mathbf{5a-d}}$, were readily soluble in common organic solvent, such as chloroform. Differential scanning calorimetry (DSC) revealed that the naphthalene bearing diamine monomers had a low entropy, and formed amorphous polyimides. They retained high moduli even at high temperatures by DMA, and had measured coefficients of thermal expansion (CTEs) in the range of 46.86–67.14 ppm by TMA. The glass transition temperature (T_g) of all polyimides were found to be 268–294°C, 298–326°C and 270–315°C, respectively by DSC, DMA, and TMA. Thermogravimetric analyses indicated that the polymers were fairly stable up to 489–571°C (10 wt% loss in N_2). They had a tensile strength in the range of 56–97 MPa, and elongations to break of around 3%. These polyimide films have dielectric constants ranging from 2.71 to 3.28 with moisture absorptions of less than 0.98%. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Pendant group; Flexible ether linkages; Solid state imidization

1. Introduction

Polyimides have a number of outstanding properties [1,2] such as high thermal resistance, dimensional stability, excellent electrical and mechanical properties. However, most polyimides suffer from processing problems due to their insolubility/infusibility. Such difficulty is due to inherent rigid macromolecular structures of their fully imidized form. Modified structures with flexible linkages between aromatic rings or with bulky pendant groups have provided improvement in solubility.[3–13] In addition, asymmetric (or zigzag) structure (e.g. *o*-terphenyldiyl [14], 2,7-triptycenediyl [15] structures) and noncoplanar (i.e. three-dimensional) structure [10,16] have also found to be quite effective in improving the solubility of polyimides. However, few reports deal with polyimides containing a naphthalene structure. Yang [17,18] had reported 2,3-naphthalene moiety and 1,5-diamino naphthalene-based polyimide, respectively. Naphthalene has also been incorporated into the backbones of many polymers including polyesters [19], polyamides [20] and bismaleimides [21,22] etc. In our previous study, [23] the incorporation of naphthalene as a pendant group in a polymer chain, has resulted in decreased crystallinity, and enhanced solubility and thermal stability.

In this study, diamine monomers with pendant naphthalene group and flexible ether linkages were synthesized and used to produce a series of novel polyimides having high thermal and dimensional stability, moisture resistance, low dielectric constant, and easy processability.

2. Experimental

2.1. Materials

All dianhydrides in high-purity were obtained from various commercial sources, such as pyromellitic dianhydride (PMDA, **6a** Chriskev), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA, **6b** Chriskev), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **6c** Chriskev), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, **6d** Aldrich), 1-naphthaldehyde (Acros), 2,6-dimethylaniline (Acros), 2,6-dimethylphenol (Acros),

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bis(4-hydroxy-3,5-dimethylphenyl)methane **2′** (Mitsui petrochemical Indus.), *p*-chloronitrobenzene (TCI), hydrazine monohydrate (Katayama), *p*-toluenesulfonic acid monohydrate (Ferak). All the reaction solvents and chemicals (or diamine monomers, such as **1**, **4**, **5** and $\mathbf{6_{a-d}}$) were used as received, then, stored over calcium hydride or in a reduced pressure dry box, they are isoquinoline (TCI), 2-methoxyethanol (Acros), *N*,*N*-dimethylacetamide (DMAc, Acros), *N*,*N*-dimethylformamide (DMF, Acros), *N*-methyl-2-pyrrolidone (NMP, Ferak), *m*-cresol (Janssen), and high-purity tetramethylammonium hydroxide (TCI).

2.2. The synthesis of bis(4-amino-3,5-dimethylphenyl)naphthylmethane (1) and bis(4-hydroxy-3,5-dimethylphenyl)naphthylmethane (2)

1 and **2** were synthesized from the reactions between 1-naphthaldehyde and 2,6-dimethylaniline or 2,6-dimethylphenol, respectively, by the methods reported in Ref. [23].

2.3. The synthesis of bis(4-nitrophenoxy-3,5-dimethylphenyl)naphthyl-methane (3)

Into a reactor equipped with a stirrer, a reflux condenser and a nitrogen inlet were charged with 26 ml of DMF, 19.86 g (0.052 mol) of **2**, 16.70 g (0.106 mol) of *p*-chloronitrobenzene, and 15.20 g (0.11 mol) of potassium carbonate. The reaction mixture was refluxed at 158–160°C for 10 h under a N_2 atmosphere. After completion of the reaction, the reaction mixture was poured into cold water to yield the crude dinitro compound, and it was collected by filtration and was further recrystallized from ethanol/water (1:1 (v/v)) to produce 26.28 g (81%) of pale-yellow crystals. m.p. 207.6°C; IR (KBr) cm^{-1}: 1355, 1516 (NO_2 str), 1233 (C–O–C str), 802 (α-nap. str); MS(EI) *m/z* 625 (M^+,95); ^1H NMR (200 MHz, $CDCl_3$) δ 2.05 (s,12H,CH_3), δ 6.18 (s,1H,α-nap. CH), δ 6.90 (s,4H,phen. H), δ 7.01–7.51 (2d,8H,phen. H), δ 7.52–8.20 (m,7H,nap. H); Anal. Calcd for $C_{39}H_{32}N_2O_6$: C, 75.00; H, 5.13; N, 4.50. Found: C, 74.41; H, 5.17; N, 4.43.

2.4. The synthesis of bis(4-aminophenoxy-3,5-dimethylphenyl)naphthyl-methane (4)

To 16.85 g (0.027 mol) of the dinitro **3** compound in 56 ml of 2-methoxyethanol, was added 0.09 g of 10% palladium on carbon (Pd/C). Over a period of 1 h, 68 ml of 80% hydrazine monohydrate was added to the above mixture at ca. 90°C and then maintained at that temperature for 11 h. After the removal of Pd/C, the hot solution was added to the water. The precipitated crude solid was recrystallized from 2-methoxyethanol/water (3:1 (v/v)) to yield 11.27 g (74%) of pale-brown powder. m.p. 214.5°C; IR (KBr) cm^{-1}: 3402, 1622 (NH str and deformation), 1219 (C–O–C str), 788 (α-nap. str); MS(EI) *m/z* 564 (M^+,100); ^1H NMR (200 MHz, DMSO-d_6) δ 2.09 (s,12H,CH_3), δ 4.67 (s,4H,NH_2), δ 6.27 (s,1H,α-nap. CH), δ 6.88 (s,4H,phen. H), δ 6.38–6.50 (2d,8H,phen. H), δ 7.01–8.04 (m,7H,nap. H); Anal. Calcd for $C_{39}H_{36}N_2O_2$: C, 82.98; H, 6.38; N, 4.96. Found: C, 82.54; H, 6.44; N, 4.95.

2.5. The synthesis of bis(4-nitrophenoxy-3,5-dimethylphenyl)methane (3′)

A mixture of bis(4-hydroxy-3,5-dimethylphenyl)methane **2′** (21.33 g, 0.083 mol), *p*-chloronitrobenzene 26.26 g (0.167 mol), potassium carbonate 23.50 g (0.17 mol), and 185 ml of DMAc was refluxed at 160°C for 8 h under nitrogen. After completion of the reaction, the reaction mixture was added to water to precipitate the product. The resulting solid was filtered and recrystallized from DMAc/acetic anhydride (1:2 (v/v)) to produce 35.13 g (85%) of light-yellow crystals. m.p. 193.8°C; IR (KBr) cm^{-1}: 1350, 1511 (NO_2 str), 1236 (C–O–C str); MS(EI) *m/z* 498 (M^+,100); ^1H NMR (200 MHz, DMSO-d_6), δ 2.06 (s,12H,CH_3), δ 3.87 (s,2H,CH_2), δ 7.12 (s,4H,phen. H), δ 6.90–7.02 (2d,8H,phen. H); Anal. Calcd for $C_{29}H_{26}N_2O_6$: C, 69.88; H, 5.22; N, 5.62. Found: C,69.43; H, 5.33; N, 5.54.

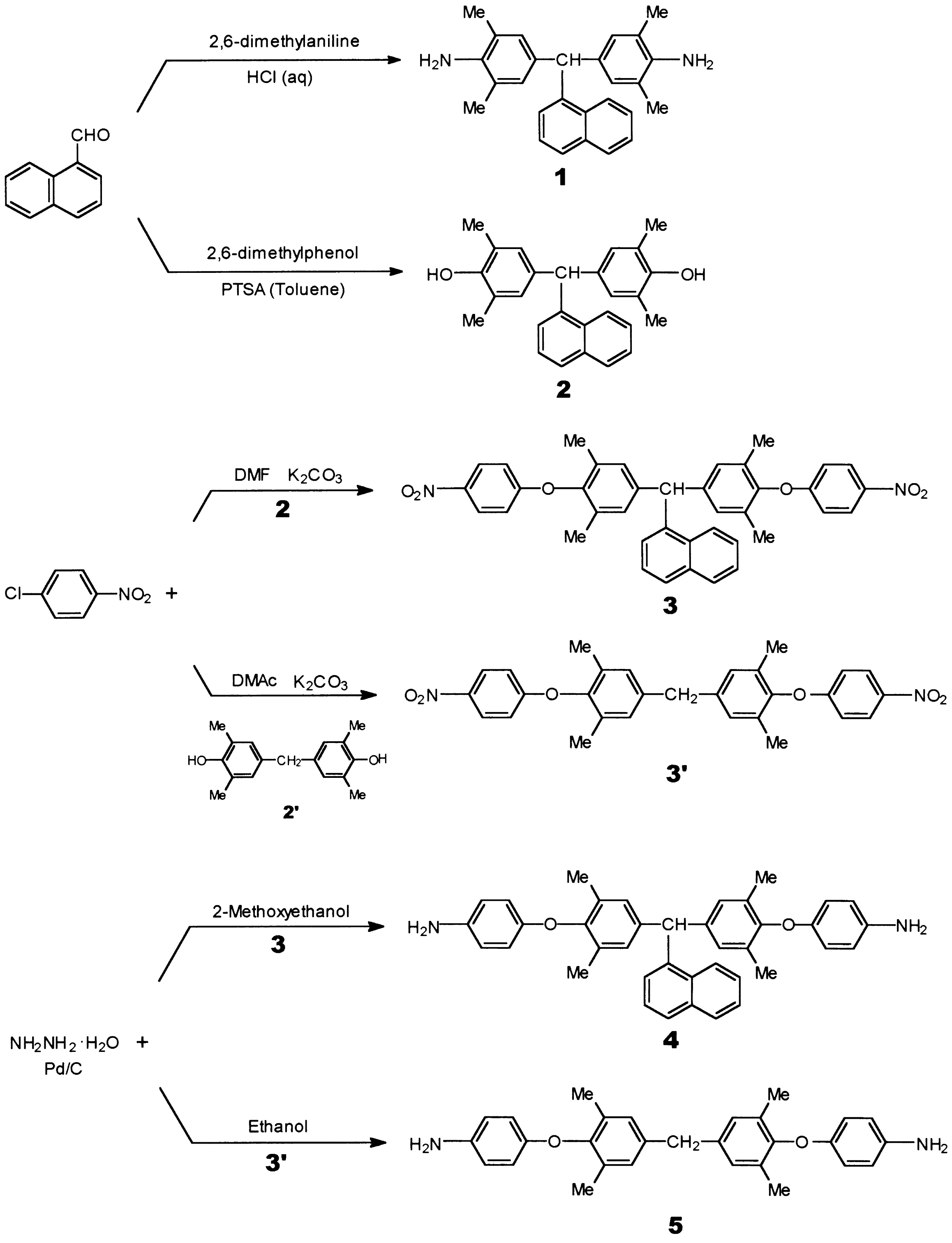
2.6. The synthesis of bis(4-aminophenoxy-3,5-dimethylphenyl)methane (5)

To a dispersion of **3′** (28.75 g, 0.058 mol) in ethanol (140 ml) was added 0.15 g of 10% Pd/C, and hydrazine monohydrate (46 ml) was charged to the stirred mixture dropwise at 70°C over 30 min. After the addition was completed, the mixture was stirred at 85°C for another 9 h. The solution was then filtered to remove Pd/C. The crude product was recrystallized from DMAc/ethanol (1:3 (v/v)) to give 19.56 g (77%) of light-white crystals. m.p. 178.1°C; IR (KBr) cm^{-1}: 3400, 1620 (NH str and deformation), 1225 (C–O–C str); MS(EI) *m/z* 438 (M^+,100); ^1H NMR (200 MHz, DMSO-d_6), δ 2.03 (s,12H,CH_3), δ 4.84(br. s,4H,NH_2), δ 3.77 (s,2H,CH_2), δ 6.97–7.09 (s,4H,phen. H), δ 6.40–6.56 (2d,8H,phen. H); Anal. Calcd for $C_{29}H_{30}N_2O_2$: C, 79.45; H, 6.85; N, 6.39. Found: C, 79.46; H, 6.90; N, 6.44.

2.7. Polymer synthesis and film casting

2.7.1. Two-step method

A three-necked flask equipped with an addition funnel and a high-purity N_2 inlet was charged with a solution of diamine **5** in DMAc, then dianhydride ($\mathbf{6_{a-d}}$) was added all at once. The mole ratio and solid content of diamine/dianhydride mixture were 1:1 and 15 wt%, respectively. The reaction mixture (ca. 30 ml) was stirred at room temperature in N_2 atmosphere affording a viscous poly(amic acid) solution after 16–18 h. A small sample of the viscous solution was taken and added to 150 ml methanol. The precipitate was collected by filtration, and then dried in vacuo to yield the solid of poly(amic acid). The remaining solution (ca. 20 ml) was spread (with film casting apparatus) on a heatproof glass plate and dried at 80°C for 4 h in a forced air oven.



Scheme 1.

The film on glass were then converted to polyimide by heating in air at 120°C for 30 min, 150°C for 30 min, 180°C for 30 min, and 300°C for 1h. The film was cooled to room temperature, and stripped from the plate by soaking in water. The average film thickness was 28 μm.

2.7.2. One-step method

Polyimides were prepared from the diamines (**1** and **4**)/ dianhydrides ($\mathbf{6}_{a-d}$) (mole ratio:1/1) in either *m*-cresol or NMP with 1–2 wt% isoquinoline as a catalyst. The solid content of the reaction mixture was maintained at 12 wt%.

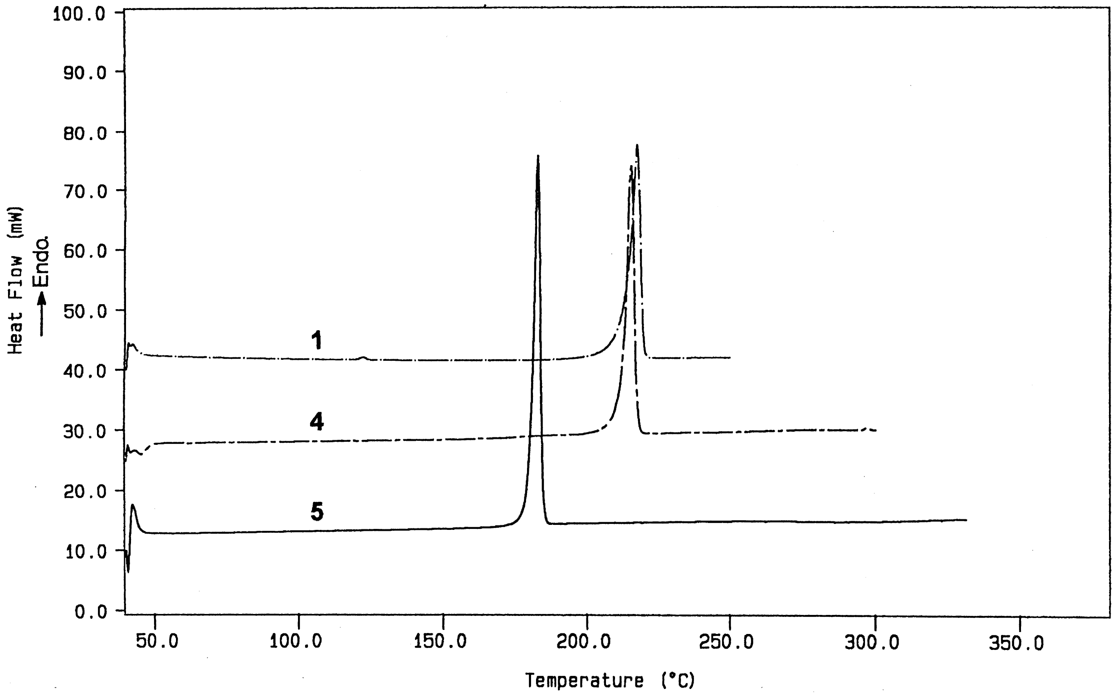
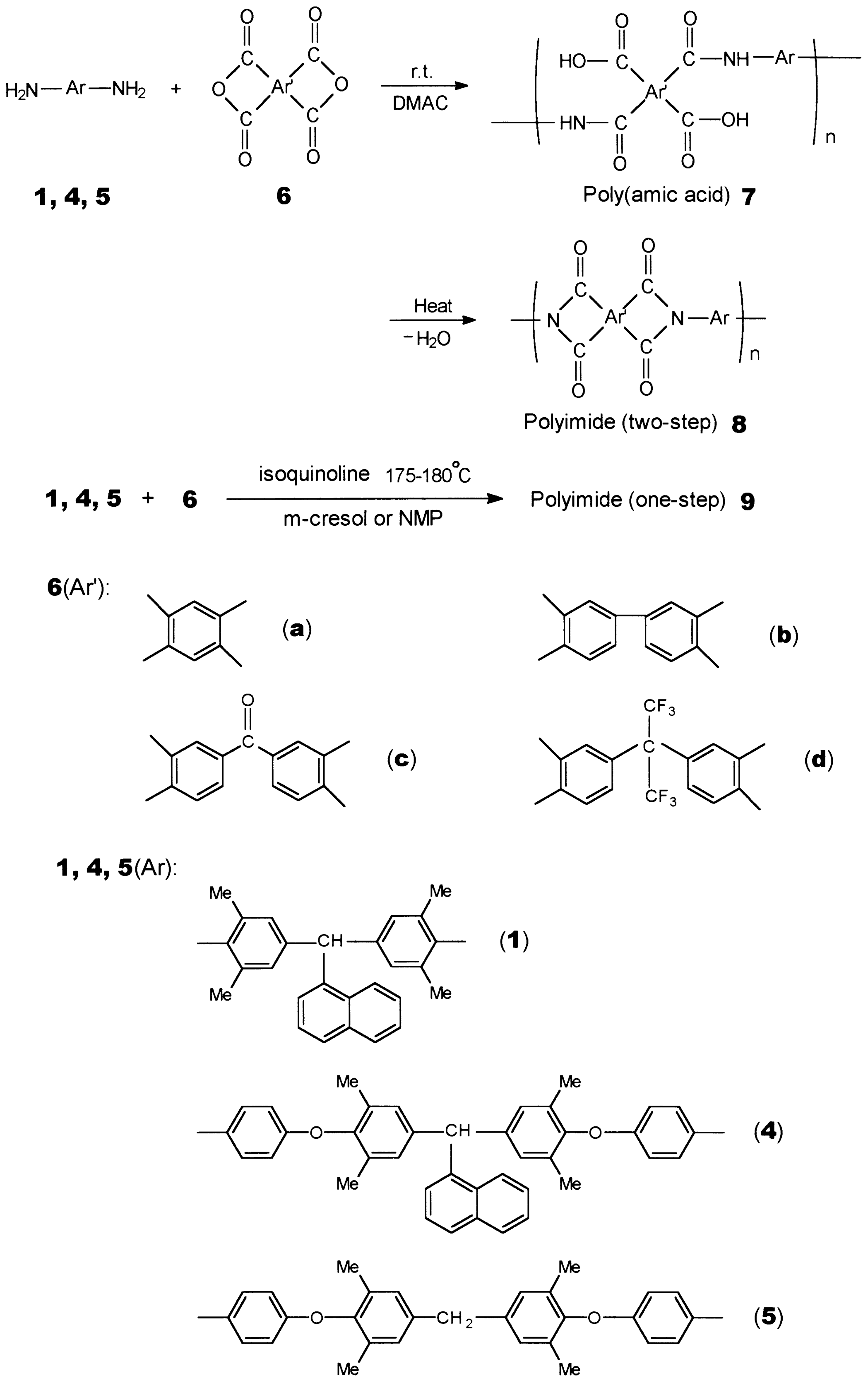


Fig. 1. DSC scans for diamine monomers.

The solution was stirred for 6 h under a N_2 atmosphere at 70°C. During this period a clear homogeneous yellow poly(amic acid) solution was formed in all cases. The reaction system was slowly heated to reflux at 175–180°C with stirring for 18 h to complete imidization. The reaction mixture was cooled and a small sample was taken and poured into methanol and the polymer was collected by filtration, and then dried in vacuo to obtain the solid of polyimide. The remaining viscous solution was spread on a glass plate. The solvent was slowly evaporated in a forced air oven at 80°C for 4 h, 120°C for 30 min, 160°C for 30 min and 200°C for 1 h. Typical film thickness was in the range of 26–40 μm.

2.8. Measurements

Fourier transform infared (FTIR) spectra were recorded on a Nicolet Magna-520 spectrometer with KBr pellets or 5–10 μm film. Spectra in the optical range of 400–4000 cm^{-1} were obtained by averaging 32 scans at a resolution of 4 cm^{-1}. ^1H NMR spectra were registered using a Bruker Analytik WP-200 spectrometer using DMSO-d_6 or $CDCl_3$ as a solvent. The ^1H chemical shifts were calibrated by using tetramethylsilane (TMS). EI (Electron Impact) source mass spectrometric analyses were performed on a VG 70-250S GC/MS spectrometer with a solid inlet. Elemental analyses were carried out with Heraeus CHN-Rapid elemental analyzer. Differential scanning calorimeter (Perkin–Elmer DSC-7) measurements were used in this study. Samples of approximately 5–6 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate of 20°C/min in the range of 40–400°C under N_2 atmosphere and the glass transition temperature (T_g) values were taken as the change of the specific heat in the heat flow curves, and peak baseline was determined from the horizontal straight method. For dynamic scanning, calibration of the calorimeter was conducted for the heating rate using an indium standard. Dynamic mechanical analysis (DMA) was performed on a Perkin–Elmer DMA-7 thermal analyzer system. A sample 15 mm length (measuring system display sample height, it was decided from sample zero), 3 mm in width, and approximately 32 μm in depth was used. The modulus and tan δ were studied when the sample was subjected to temperature scan mode with a extension measuring system (use stainless steel extension kit) at a programmed heating rate of 10°C/min from 30–360°C in a frequency of 1 Hz. The coefficient of thermal expansion (CTE) was measured with TMA mode (use quartz extension kit) of Perkin–Elmer DMA-7 thermomechanical analyzer (10°C/min, 30–360°C and 2 mN tension). The thermal expansion increased with temperature and the CTE values were calculated from the slope in front of T_g. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA-7 thermal analyzer using a heating rate of 20°C/min in N_2 at a purge pressure of 25 psi within the temperature range of 30–800°C. The inherent viscosities of the polyimides in concentrated NMP or H_2SO_4 solutions (conc. 0.5 g/dl) were measured at 30°C with a Ubbelohde viscometer. The dielectric constants were determined by the bridge method with Du pont-2970 dielectric analyzer at a frequency of 1 KHz, 300 N, and 30°C in a N_2 atmosphere at a flow rate of 500 cm^3/min by


H2N—Ar—NH2
+
Ar'
r.t.
DMAC
1, 4, 5
6
HO—C
C—NH—Ar
HN—C
C—OH
n
Poly(amic acid) 7
Heat
-H2O
N
N—Ar
Polyimide (two-step) 8
1, 4, 5 + 6
isoquinoline 175-180°C
m-cresol or NMP
Polyimide (one-step) 9
6(Ar'):
(a)
(b)
(c)
(d)
CF3
1, 4, 5(Ar):
Me
CH
CH2
O
(1)
(4)
(5)

Scheme 2.

Table 1
Synthesis of polyimides form various diamines and various aromatic tetracarboxylic dianhydrides

Polymer	Preparation	Solvent	Solid (wt%)	η_{inh} (dl/g)[a]	Id (%)[b]	Film
$\mathbf{8}_{\mathbf{5a}}$	Two-step	DMAc	15	–[c]	–	Clear
$\mathbf{8}_{\mathbf{5b}}$	Two-step	DMAc	15	–	–	Clear
$\mathbf{8}_{\mathbf{5c}}$	Two-step	DMAc	15	–	–	Clear
$\mathbf{8}_{\mathbf{5d}}$	Two-step	DMAc	15	–	–	Clear
$\mathbf{9}_{\mathbf{1a}}$	One-step	*m*-Cresol	12	0.68[d]	94.56[e]	
$\mathbf{9}_{\mathbf{1b}}$	One-step	*m*-Cresol	12	0.72	95.04	Clear
$\mathbf{9}_{\mathbf{1c}}$	One-step	*m*-Cresol	12	0.76	97.17	Clear
$\mathbf{9}_{\mathbf{1d}}$	One-step	*m*-Cresol	12	0.54	92.29	Clear
$\mathbf{9}_{\mathbf{4a}}$	One-step	NMP	12	0.48	90.45	Clear
$\mathbf{9}_{\mathbf{4b}}$	One-step	NMP	12	0.55	93.41	Slig. hazy
$\mathbf{9}_{\mathbf{4c}}$	One-step	NMP	12	0.62	94.03	
$\mathbf{9}_{\mathbf{4d}}$	One-step	NMP	12	0.51	91.22	Clear

[a] 0.5 g/dl in concentrated NMP at 30°C.
[b] Adapted from Ref. [25]; the sample is soluble in NMP.
[c] Cannot measured (because of the polyimides $\mathbf{8}_{5a-d}$ were almost insoluble in any solvent, see Table 2).
[d] 0.5 g/dl in concentrated H_2SO_4 at 30°C.
[e] Adapted from Ref. [25]; the sample is soluble in chloroform.

the two parallel plate mode. The specimens were subjected to vacuum pretreatment of 1–3 mm Hg at 100°C for 2 h to eliminate the absorbed water. The amount of moisture absorption was measured by immersing specimens in 30°C water for 96 h, and the weight difference after aging was determined. The degree of imidization (I_d) was obtained from a MCI B3-109 automatic potentiometric titrator, by the acid–base potentiometric titration of the corresponding poly(amic acid). A solution of tetramethylammonium hydroxide dissolved in absolute methanol was used as a titrant, and the end points were detected by the first derivative of the potential versus the volume of the titrant. Mechanical properties of the film were measured in accordance with ASTM-D638, D882 on an Instron HT-8504A (cross-head speed: 5 mm/min). Measurement was performed at 30°C with film specimens (height: 60 mm, width: 13.5 mm), and an average of at least four individual determinations was used.

3. Results and discussion

3.1. Monomer synthesis

Scheme 1 shows the synthetic routes to **1**, **4**, and **5**. The high yield (after recrystallization of more than 80%) of **3** and **3′** can be attributed to the fact that the dipotassium salt of **2** and **2′** are good nucleophiles, because of the electron donating effect of dialkyl substituents at ortho positions to OH is greater than their steric hindrance [24]. In addition, the electron withdrawing NO_2 group in *p*-chloronitrobenzene also increases its reactivity. The structures of diamine monomers were confirmed by ^{1}H NMR spectra, mass spectrometry, IR spectra, elemental analysis and DSC (Fig. 1), and were in good agreement with the proposed structures.

3.2. Preparation of polymers

Novel polyimides containing naphthalene side group were synthesized by conventional two-step and one-step methods starting from diamines **1**, **4**, and **5** with aromatic tetracarboxylic dianhydrides **6** through ring-opening polyaddition and subsequent thermal cyclodehydration or chemical imidization, as shown in Scheme 2. In this study, a two-stage imidization followed by solid state imidization (the **8**-series) and a one-pot polymerization with solvent-thermal imidization (the **9**-series) were investigated. The **1** and **4** (containing naphthalene side group) series of polymers which cannot be made by the two-stage method because of the low reactivity (due to the naphthalene structure and at a low reaction temperature) were synthesized by one-step method. **5** (non-naphthalene containing monomer) series of polymers were not made by a one-pot method which is due to the solubility problem (precipitation of polymer). Poly(amic acid) formation is actually a very complex situation which includes the competition between propagation and hydrolysis. According to the Carother’s equation, in order to obtain a high molecular weight poly(amic acid), the monomer purity and solvent dryness are extremely critical. In addition, the process of monomer addition also plays an important role in successful polymerization [17,18]. Table 1 summarizes the resulted polyimides. The polyimides **9** had inherent viscosities between 0.48 and 0.76. In fact, the η_{inh} values were lower than those of the general polyimides, which may be due to higher solution polymer chain mobility and is different for their polymers with the bulky naphthalene substituent dangling from the main chain. The degree of imidization of poly(amic acid)s was estimated by the acid–base potentiometric titration, [25] and can be followed by NMR spectrometry for the disappearance of the COOH proton in the poly(amic acid) at 11 ppm [26] The imidization fraction is calculated by the

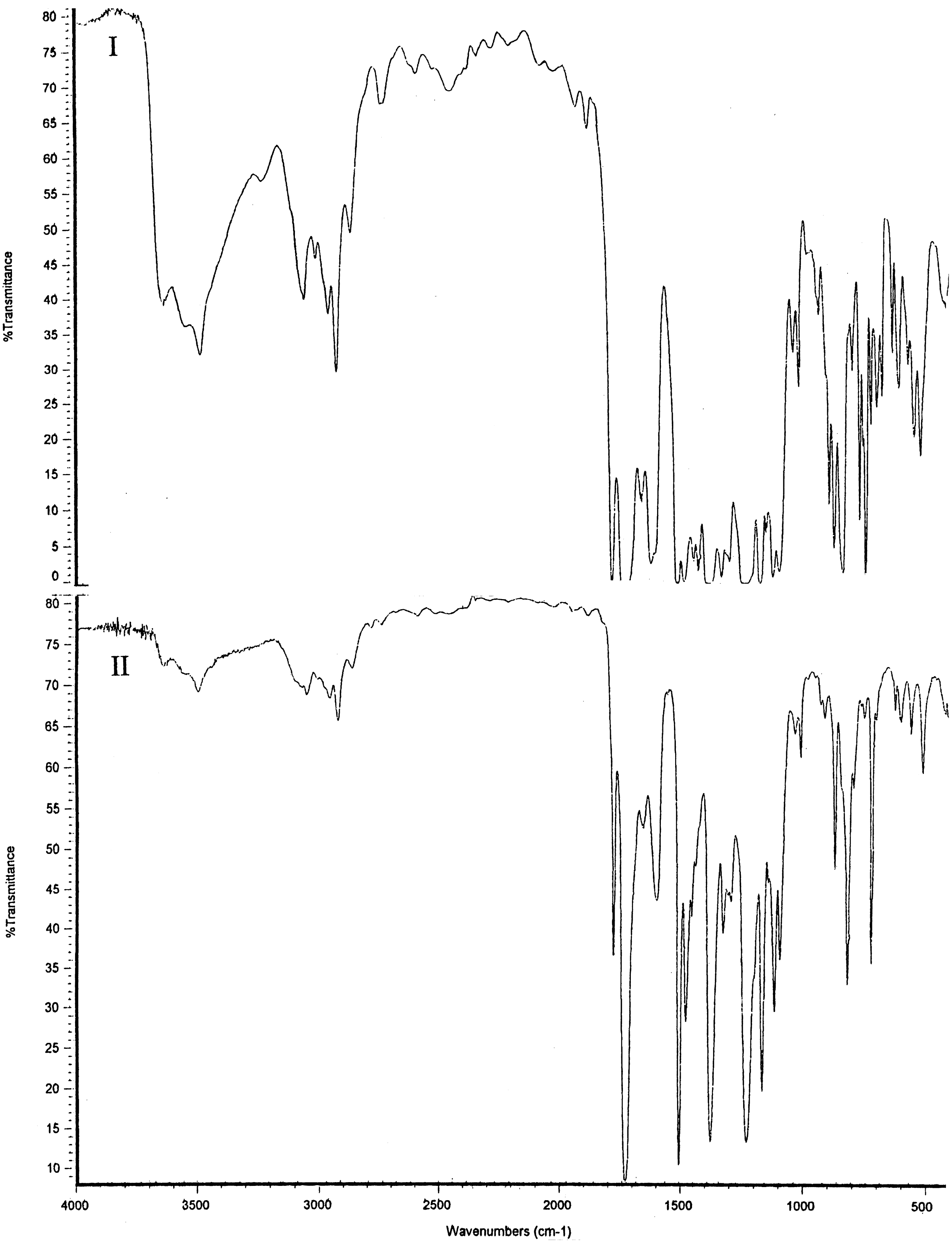


Fig. 2. FTIR spectra of **5a** poly(amic acid) (I) and corresponding polyamide (II) by the two-step method.

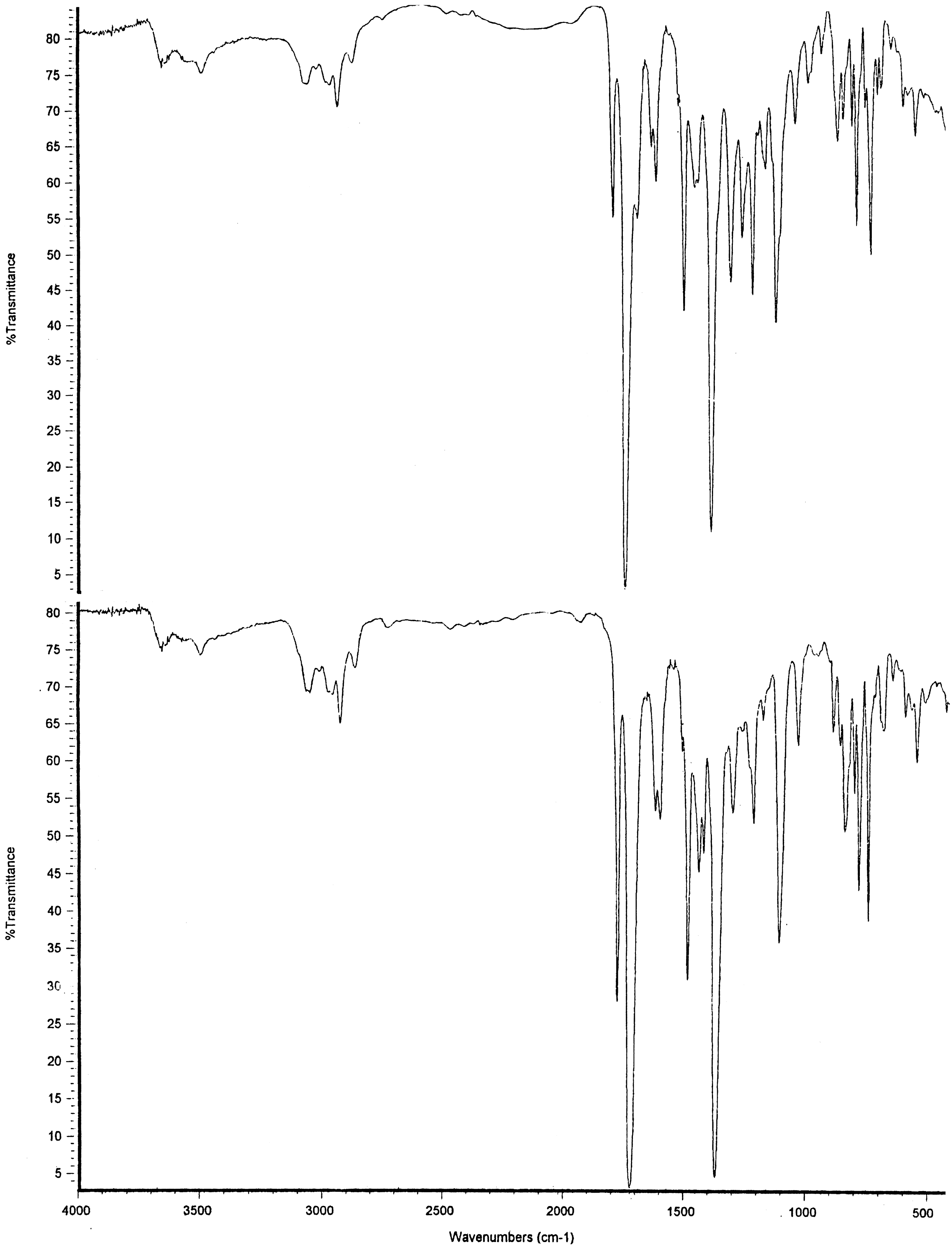


Fig. 3. FTIR spectra of polyimide $\mathbf{9}_{1b}$: top, the viscous solution was poured into MeOH, and then dried in vacuo to obtain the product; bottom, the viscous solution was cast onto a glass plate, and dried to obtain the film; in one-step procedure.

Table 2
Solubility of polyimides ((+ +) soluble at room temperature. (− −) insoluble in hot solvent; (h +) soluble in hot solvent (at 60–70°C); (h −) swelled or slightly soluble in hot solvent; (±) soluble at room temperature, but a few residual carbon was observed, measured at a concentration of 1.0 g/dl in solvent)

Polymer	Solvent							
	m-Cresol	Pyridine	1,4-Dioxane	Chloroform	THF	DMF	NMP	H_2SO_4
$\mathbf{8}_{5a}$	− −	− −	− −	− −	− −	− −	− −	±
$\mathbf{8}_{5b}$	− −	− −	− −	− −	− −	− −	− −	±
$\mathbf{8}_{5c}$	− −	− −	− −	− −	− −	− −	− −	±
$\mathbf{8}_{5d}$	− −	− −	− −	− −	− −	− −	− −	±
$\mathbf{9}_{1a}$	h −	h −	h −	+ +	h −	h −	h −	+ +
$\mathbf{9}_{1b}$	h −	h +	− −	+ +	h −	h +	h +	+ +
$\mathbf{9}_{1c}$	h +	+ +	h +	+ +	+ +	+ +	+ +	+ +
$\mathbf{9}_{1d}$	h +	+ +	h +	+ +	+ +	+ +	+ +	+ +
$\mathbf{9}_{4a}$	h +	h +	h +	+ +	+ +	+ +	+ +	+ +
$\mathbf{9}_{4b}$	h +	+ +	h +	+ +	+ +	h +	+ +	+ +
$\mathbf{9}_{4c}$	h +	+ +	h +	+ +	+ +	+ +	+ +	+ +
$\mathbf{9}_{4d}$	h +	+ +	h +	+ +	+ +	+ +	+ +	+ +

ratio of COOH protons/all aromatic protons $= 0.01(1 - x)/4$ (x: imidization fraction) [27]. If the poly(amic acid) is completely converted into polyimide, the imidization fraction is close to 1. There is only a slight difference between titration and NMR methods. Fig. 2 shows the IR spectra [28–30] of the representative poly(amic acid) $\mathbf{7}_{5a}$ and the corresponding polyimide $\mathbf{8}_{5a}$. In spectrum (I), which corresponds to poly(amic acid), the absorption at 3100–3450 cm^{-1} is due to the stretching of OH and NH, and the absorption at 1550–1650 cm^{-1} is due to secondary amide group. In spectrum (II), which represents the polyimide structure, the absorption at 1780 and 1725 cm^{-1} are related to symmetric and asymmetric C=O of imide group, respectively, while the absorption at 1100 and 720 cm^{-1} are the vibrations of imide structure, and the absorption at 1390 cm^{-1} is C–N groups. The IR spectra of Fig. 3 (top and bottom) were almost identical indicating a rather complete imidization during the one-step method.

Table 3
Thermal properties of polyimides

	T_g(°C)			T_d(°C)	Char yield
Polymer	DSC	DMA	TMA	10 wt% loss in N_2	800°C (%)
$\mathbf{8}_{5a}$	–	312	287	502	61.82
$\mathbf{8}_{5b}$	282	310	291	496	55.91
$\mathbf{8}_{5c}$	278	303	289	494	59.09
$\mathbf{8}_{5d}$	274	298	287	491	57.27
$\mathbf{9}_{1a}$	–			571	63.73
$\mathbf{9}_{1b}$	294	326	315	564	67.64
$\mathbf{9}_{1c}$	287	318	304	520	62.55
$\mathbf{9}_{1d}$	277	314	286	503	58.26
$\mathbf{9}_{4a}$	280	315	292	501	52.82
$\mathbf{9}_{4b}$	293	–	286	497	51.69
$\mathbf{9}_{4c}$	272			489	48.45
$\mathbf{9}_{4d}$	268	308	270	492	46.62

3.3. Characterization of polyimides

The solubilities of polyimides in various solvents were investigated and the results are summarized in Table 2. Polyimides $\mathbf{8}_{5a-d}$ are soluble only in concentrated sulfuric acid, and $\mathbf{9}_{1a-d}$ exhibited somewhat limited solubility. However, $\mathbf{9}_{4a-d}$ show better solubility compared to the others. Although, the molecular structure of polyimides $\mathbf{8}_{5a-d}$ and $\mathbf{9}_{4a-d}$ were similar, but the molecular volumes (evaluated from density, see Table 4) were different, $\mathbf{8}_{5a-d}$ packed denser than $\mathbf{9}_{4a-d}$; also, they had a smaller molecular space which led to a decrease in solubility. Due to the introduction of a bulky naphthalene side group and flexible ether segments into the polyimides $\mathbf{9}_{4a-d}$, they have exhibited an excellent solubility toward test solvents. The polyimides possess ketone [17], hexafluoroisopropylidene [31] units between two phthalimide units exhibited high solubility, because of the electronic polarizability of its carbonyl group and hexafluoroisopropylidene groups which hindered the interaction between neighboring molecules.

The thermal properties of the polyimides were investigated by TGA, DSC, DMA, and TMA, as shown in Table 3. The results of the TGA analyses showed an excellent thermal stability of the synthesized polyimides. The 10 wt% losses in N_2 atmosphere were 489–571°C, and the char yields at 800°C in N_2 atmosphere were higher than 46%; the polyimide $\mathbf{9}_{1b}$ had the highest char yield of up to 68%. These results suggest a high thermal stability of the stiff naphthalene structure. No endothermic peaks above their glass transition temperatures were observed in DSC scans, which may be attributed to the amorphous molecular structure for all polyimides. Moreover, the polyimides of $\mathbf{9}_{1a-d}$ exhibited higher T_g than $\mathbf{9}_{4a-d}$ which may be attributed to its rigid structure (without ether linkage).

Physical and mechanical properties of the polyimides were shown in Table 4. Moisture absorptions of naphthalene containing polyimides were noticeably low. Furthermore,

Table 4
Physical and mechanical properties of polyimides (ρ: bulk density of polymer; MA: moisture absorption; DC: dielectric constant)

Polymer	ρ (g/ml)	MA (%)	DC	Tensile stress (MPa)	Elongation (%)	Mod. (GPa)	CTE (ppm)
8$_{5a}$	1.3503	0.804	3.04	91.98	4.38	2.69	62.52
8$_{5b}$	1.3138	0.785	3.15	74.35	3.48	3.18	62.69
8$_{5c}$	1.2957	0.971	3.28	81.03	4.08	3.03	63.20
8$_{5d}$	1.2859	0.547	2.97	65.58	2.40	3.22	67.14
9$_{1a}$	1.2697	–	–	–	–	–	–
9$_{1b}$	1.2599	0.616	2.78	97.01	3.04	4.02	48.74
9$_{1c}$	1.2381	0.728	2.84	86.29	3.44	4.05	54.78
9$_{1d}$	1.2478	0.329	2.71	63.77	2.16	4.21	59.48
9$_{4a}$	1.2684	0.658	2.86	83.54	3.52	3.28	46.86
9$_{4b}$	1.2430	0.762	2.90	75.91	2.76	3.14	56.52
9$_{4c}$	1.2382	–	–	–	–	–	–
9$_{4d}$	–	0.485	2.82	55.72	2.2	3.81	58.20

for the same diamine, the fluoropolymers exhibited ca. 50% lower moisture absorption than polyimides without fluorine. Dielectric constants were also noticeably low for naphthalene containing polymers. All polyimides have dielectric constant values much lower than that of standard KAPTON (ca. 3.5).

The mechanical properties were determined via an Instron machine. The polyimide films had tensile strengths of 55.72–97.01 MPa, elongations at break of 2.16–4.38%, and initial moduli of 2.69–4.21 GPa. Elongation to break values of all the polyimides, except fluorine containing polyimides (such as **8**$_{5d}$, **9**$_{1d}$, and **9**$_{4d}$) had moderate values. The modulus values observed in these polyimides were comparable to those with very stiff structures, and because of this high stiffness they provide films with high in-plane orientation. The coefficients of thermal expansion (CTEs) were in the range of 46.86–67.14 ppm. In general, the polyimides, which contained planar naphthalene structure showed low CTE values. In addition, the dianhydride also had an effect on the CTE observed, the more rodlike dianhydrides yielding lower CTEs.

4. Conclusion

The combination of the special features of naphthalene structure (rigid, bulky, moisture resistance, and low coefficient of thermal expansion) with that of polyimide (thermal stability, good mechanical and electrical properties) has resulted in novel polyimides with excellent properties and processability. This study of the one-step method was used to prepare polyimides, which cannot be made by the two-step method. However, the premature precipitation of polyimide oligomer may occur in the one-step method [32]. Fortunately, the results of the present study were quite satisfactory.

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