Synthesis and Characterization of New Soluble and Thermally Stable Poly(Amide-Imide)s Containing Pendent Benzimidazole Moieties

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ABSTRACT: Preparation of new types of poly(amide-imide)s with high thermal stability and improved solubility was investigated. Two new diimide-dicarboxylic acid containing pendent benzimidazole group, viz., 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl] benzimidazole (DIDA-i) and 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl] 5-methyl benzimidazole (DIDA-ii) from the condensation of 5-(2-benzimidazole)-1,3-phenylenediamine (DABI$_A$) and 5-(5-methyl-2-benzimidazole)-1,3-phenylenediamine (DABI$_B$) with trimellitic anhydride in glacial acetic acid were synthesized, respectively. 1,3-bis(*N*-trimellitimidoyl)benzene (DIDA-iii, as a reference) was also synthesized in a similar manner to study the properties of the its structure. Three series of aromatic poly(amide-imide)s were prepared by triphenyl phosphite-activated polycondensation from diimide-dicarboxylic acid DIDA-i, DIDA-ii, and the reference monomer DIDA-iii with various aromatic diamines. The polymers were obtained in quantitative yields with inherent viscosities between 0.46 and 0.81 dL g^{-1}. The effects of the benzimidazole pendent groups on the polymer properties, such as solubility and thermal stability were investigated by comparison of the polymers. The polymers bearing benzimidazole pendent groups exhibited thermal stability and good solubility in common polar solvents higher than the reference polymers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 185–192, 2009

Key words: polycondensation; thermal properties; structure-property relation; poly(amide-imide)s; benzimidazole

INTRODUCTION

Polyimides have been used extensively in the aerospace and electronics fields because of their thermal stability and excellent mechanical and electrical properties. Usually, polyimides are difficult to fabricate because of their infusibility and insolubility in most organic solvents.[1] These properties make them generally intractable or difficult to process, thus limiting their applications. Therefore, incorporating new functionalities to make polyimides more tractable without deteriorating their own excellent properties has become one important target of polyimide's chemistry.[2–5] It has been generally recognized that flexible linkages[6,7] or the bulky lateral groups[8–11] impart better solubility and melt-processing characteristics compared with polymers without these linkages. However, the attachment of bulky pendent benzimidazole groups can impart an increase in T_g by restricting the segmental mobility, while providing an enhanced solubility because of decreased packing density and crystallinity.[12,13]

Various synthetic methods for the preparation of poly(amide-imide)s (PAIs) have been disclosed in many reports. One of the convenient and efficient synthesis of high-molecular weight PAIs is the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines by means of the Yamazaki–Higashi phosphorylation technique,[14] developed by one of us.[15,16] The direct polycondensation route is a very useful laboratory method and avoids using moisture-sensitive acid chlorides or isocyanates.[17–19] To synthesize PAI generally involves use of trimellitic anhydride, TMA, as a major component, where TMA is first reacted with a specific diamine to synthesize a diimide-dicarboxylic acid (DIDA), and then DIDA is reacted with various aromatic diamines to synthesize a series of alternative copolymers of PAIs.

In this study, we report the synthesis and characterization of two series of new PAIs containing the pendent benzimidazole group [PAI-i(a-f)] and [PAI-ii(a-f)] derived from DIDA-i and DIDA-ii with various aromatic diamines (a–f). The effect of the benzimidazole pendent group on the polymer properties such as solubility and thermal stability is also investigated by comparison with PAIs missing benzimidazole pendent group [PAI-iii(a-f)], (reference PAIs), obtained from DIDA-iii and the same diamines.

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EXPERIMENTAL

Materials

All chemicals were purchased from Merck (Darmstadt, Germany) and Fluka Chemical Co. (Buchs, Switzerland). Trimellitic anhydride (TMA), triphenylphosphite (TPP), and polyphosphoric acid (PPA) were used as received and were used without further purification. N-methyl-2-pyrrolidone (NMP) was distilled over CaH_2, pyridine was dried in KOH pellets and stored over 4°A molecular sieves. Commercially obtained calcium chloride was dried under vacuum at 180 to 200°C for 8 h before each run. Aromatic diamines, including o-phenylenediamine, p-phenylenediamine (c), and 1,3-diaminobenzoic acid were recrystallized from ethanol. m-Phenylenediamine (a), 2,6-diaminopyridine (b) were purified by sublimation before use. Glacial acetic acid (purity > 99%) was purchased from Merck and was used without further purification.

Synthesis of the monomers

5-(2-Benzimidazole)-1,3-phenylenediamine ($DABI_A$)

In a 250 mL three-neck round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, outlet $CaCl_2$ drying tube, a thermometer, and oil bath was charged with 90 g of polyphosphoric acid (PPA), 5.9 g (0.055 mol) of 1,2-phenylenediamine, and 7.6 g (0.05 mol) of 3,5-diaminobenzoic acid and with stirring under nitrogen atmosphere. The reaction mixture was heated at 120°C for 8 h. The reaction temperature was increased to 190°C and held at this temperature for an additional 15 h. After cooling to room temperature, the slurry was poured in to 300 mL of water. The brown solid obtained was filtered off, washed thoroughly with water, then with dilute $NaHCO_3$ and finally with water (8.2 g, yield 73%). The products recrystallized from a mixture of DMF/water (1 : 2 v/v); m.p.: 246–247°C (lit.[20] 242–243°C).

5-(5-Methyl-2-benzimidazole)-1,3-phenylenediamine ($DABI_B$)

$DABI_B$ was synthesized with the same procedure as $DABI_A$ from 4-methyl-1,2-phenylenediamine instead of 1,2-phenylenediamine and 3,5-diaminobenzoic acid. The obtained light-brown solid was recrystallized from water. Yield: 68% (8.1 g); m.p.: 191–193°C.

2-[3,5-bis(N-trimellitimidoyl)phenyl] benzimidazole (DIDA-i)

To a 250 mL round-bottom flask fitted with a magnetic stirrer and a reflux condenser were added 2.24 g (0.01 mol) of $DABI_A$, 4.80 g (0.024 mol) of trimellitic anhydride, and 45 mL glacial acetic acid. The

heterogeneous mixture was refluxed for 15 h. The reaction mixture was filtered to yield a yellow-brown solid, which was rinsed with ethanol to remove excess acetic acid. The crude product obtained was washed several times with ethanol and then purified by recrystallization from DMF, and dried under vacuum at 100°C for 12 h to afford 5.20 g (91%) of DIDA-i as a yellow-brown solid (m.p. > 300°C).

The other monomers, 2-[2,3-bis(N-trimellitimidoyl) phenyl] 5-methyl benzimidazole (DIDA-ii) (yield, 84%; m.p. > 300°C) and 1,3-bis(N-trimellitimidoyl) benzene (DIDA-iii, as a reference) (yield, 94%; m.p. > 300°C), were synthesized in a procedure similar to that mentioned earlier. The spectroscopic data for these monomers are shown in Table I.

Polymer synthesis

A typical synthesis procedure of coPAIs was as follow. A mixture of 0.372 g (0.65 mmol) of DIDA-i and 2.5 mL NMP was stirred under nitrogen gas and heated to 70°C to dissolve DIDA-i. Pyridine (0.6 mL), 0.7 mL TPP, and 0.25 g calcium chloride were added to the reaction mixture. The mixture was stirred and heated to 110°C. An equal molar amount of diamine **a** (0.070 g, 0.65 mmol) was then added to this mixture. The resulting mixture was reacted at 110°C for 5 h. More NMP (~2.5 mL) was added during the polymerization to maintain the viscosity of the reaction mixture, and allowed the solution to be stirred. After the completion of polymerization, the viscous mixture was poured into methanol. The precipitated polymer was filtered and washed thoroughly with methanol and hot water and then dried under a vacuum to give 0.39 g (92%) of PAI-**ia**. The inherent viscosity of polymer, PAI-ia, was 0.75 dl g^{-1} measured at a concentration of 0.5 g/dL in N,N-dimethylacetamide (DMAc) at 30°C. Elemental analysis: calculated for $C_{37}H_{20}N_6O_6$ (644.61)$_n$: C (68.94%); H (3.13%); N (13.04%). Found, C (67.96%); H (2.93%); N(12.73%).

The other PAIs were synthesized by an analogous procedure described earlier.

Inherent viscosity, λ_{max} value and yields of PAIs were summarized in Table II. The spectroscopic data for the PAIs are discussed in Results and Discussion section.

Measurements

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AV-500 FT-NMR spectrometer in DMSO-d_6 at 25°C with frequencies of 500.13 and 125.77 MHz for the ^{1}H and ^{13}C spectra, respectively. Ultraviolet maximum wavelength (λ_{max}) values were obtained in DMSO at a concentration of 0.1 mg mL^{-1} at 25°C using a Shimadzu Multispec-1501 spectrometer.

TABLE I
^{1}H-NMR, ^{13}C-NMR, FTIR, and Mass Spectral and Elemental Analysis of Monomers

Code	Spectral data
DABI$_A$	^{1}H-NMR (DMSO-d_6): 12.46 (1H, NH), 7.63, 7.20 (4H, aromatic of benzimidazole segment), 6.60, 5.91 (3H, aromatic of 1,3-phenylenediamine ring), 4.86 (4H, NH$_2$); ^{13}C-NMR (DMSO-d_6): 152.61, 149.11, 136.67, 129.39, 123.40, 114.67, 102.85, 102.03 ppm; FTIR (KBr, cm^{-1}): 3347−3219, 1615, 1485, 1253, 1071, 878, 748; m/z: 224 [M$^+$]; elemental analysis: calculated for C$_{13}$H$_{12}$N$_4$: C, 69.62; H, 5.39; N, 24.98; Found: C, 69.67; H, 5.28; N, 24.88.
DABI$_B$	^{1}H-NMR (DMSO-d$_6$): 12.51 (1H, NH); 7.71, 7.38 (3H, aromatic of benzimidazole segment), 6.61, 5.94 (3H, aromatic of 1,3-phenylenediamine ring), 4.84 (4H, NH$_2$), 2.48 (3H, CH$_3$); ^{13}C-NMR (DMSO-d_6): 152.43, 149.23, 137.87, 131.10, 130.64, 122.98, 114.67, 114.11, 101.79, 101.47, 21.24 ppm; IR (KBr, cm^{-1}): 3386−3219, 1610, 1491, 1258,1074, 874; m/z: 238 [M$^+$]; elemental analysis: calculated for C$_{14}$H$_{14}$N$_4$: C, 70.57; H, 5.92; N, 23.51; Found: C, 70.06; H, 5.73; N, 24.03.
DIDA-i	^{1}H-NMR (DMSO-d$_6$): 13.34 (broad, carboxylic acid O-H and N-H), 8.44 (d, 2H), 8.41 (s, 2H), 8.35 (s, 2H), 8.13 (d, 2H), 7.78 (s, 1H), 7.62 (d, 2H), 7.23 (m, 2H); ^{13}C-NMR (DMSO-d_6): 165.98, 165.96, 165.77, 151.12, 149.49, 136.71, 135.60, 134.78, 132.86, 131.97, 131.51, 129.60, 126.64, 124.63, 123.92, 123.53, 122.51 ppm; FTIR (KBr, cm^{-1}): 3483−2500, 1782, 1720, 1612, 1350, 1087,933, 871, 725; m/z: 572 [M$^+$]; elemental analysis: calculated for C$_{31}$H$_{16}$N$_4$O$_8$: C, 65.04; H, 2.82; N, 9.79; found: C, 64.56; H, 2.73; N, 9.83.
DIDA-ii	^{1}H-NMR (DMSO-d$_6$): 13.14 (broad, carboxylic acid O−H and N−H), 8.44(d, 2H); 8.37(d, 2H); 8.12(d, 2H); 7.93 (s, 2H); 7.75 (s, 1H); 7.51 (d, 1H); 7.39 (s, 1H); 7.05 (d, 1H); 2.42 (s, 3H); ^{13}C-NMR (DMSO-d_6): 165.94, 165.92, 165.75, 152.14, 149.11, 136.79, 135.54, 134.71, 134.64, 132.79, 131.93, 131.63, 129.61, 126.44, 125.43, 124.48, 123.86, 123.47, 122.57, 122.46, 21.25 ppm; FTIR (KBr, cm^{-1}): 3444−2500, 1782, 1728, 1612, 1342, 1087, 918, 864, 725; m/z: 586 [M$^+$]; elemental analysis: calculated for C$_{32}$H$_{18}$N$_4$O$_8$: C, 65.53; H, 3.09; N, 9.55; found: C, 65.06; H, 2.83; N, 10.03.
DIDA-iii	^{1}H-NMR (DMSO-d$_6$): 12.89 (broad, carboxylic acid O-H); 8.43 (d, 2H), 8.14 (s, 2H), 7.98 (d, 2H), 7.85 (s, 1H), 7.43 (m, 2H), 7.22 (m, 1H); ^{13}C-NMR (DMSO-d_6): 166.65, 166.62, 165.84, 140.24, 139.48, 135.44, 134.14, 132.82, 131.94, 129.51, 127.22, 126.31, 123.37 ppm; FTIR (KBr, cm^{-1}): 3700−2500, 1782, 1728, 1605, 1583, 1489, 1470, 1363, 1238, 1101, 865, 725; m/z: 456 [M$^+$]; Elemental analysis: calculated for C$_{24}$H$_{12}$N$_2$O$_8$: C, 63.16; H, 2.63; N, 6.14; Found: C, 62.81; H, 2.71; N, 6.03.

FTIR spectra were recorded on a Shimadzu FTIR-8300 spectrometer for the measurement of infrared absorption spectra for monomers and polymers. The spectra of solids were obtained using KBr pellets. Melting points (m.p.) were determined with a Buchi 535 melting point apparatus. The average molecular

TABLE II
Some Characterization Data and Solubility of the PAIs

| code	Yield (%)	η_{inh}[a] (dL/g)	λ_{max}[b] (nm)	M_w[c] ($\times 10^4$)	M_w/M_n	Solvent DMAc	DMSO	DMF	NMP	THF	Py	H$_2$SO$_4$	m-Cresol	CF
PAI-ia	92	0.75	305	3.98	1.4	++	+	++	++	−	±	++	+	−
PAI-ib	89	0.81	312	4.01	1.5	++	++	++	++	−	±	++	+	−
PAI-ic	93	0.65	307	−	−	++	+	+	+	−	−	++	−	−
PAI-id	87	0.72	315	4.21	1.6	++	+	++	++	−	±	++	±	−
PAI-ie	81	0.57	317	3.87	1.7	++	++	++	++	±	++	++	++	±
PAI-if	78	0.51	319	3.84	1.6	++	++	++	++	±	++	++	++	±
PAI-iia	88	0.73	306	4.41	2.1	++	++	++	++	−	±	++	+	−
PAI-iib	90	0.79	312	4.39	1.7	++	++	++	++	−	±	++	+	−
PAI-iic	92	0.61	306	−	−	++	+	+	++	−	−	++	−	−
PAI-iid	86	0.67	315	3.90	1.6	++	++	++	++	−	+	++	+	−
PAI-iie	79	0.55	317	4.27	1.5	++	++	++	++	±	++	++	++	±
PAI-iif	72	0.46	318	3.73	1.7	++	++	++	++	±	++	++	++	±
PAI-iiia	92	−[d]	298	−	−	+	±	±	+	−	−	++	±	−
PAI-iiib	91	−[d]	301	−	−	+	±	+	+	−	−	++	±	−
PAI-iiic	95	−[d]	292	−	−	±	−	±	−	−	−	+	−	−
PAI-iiid	88	0.81	303	−	−	++	+	+	+	−	±	++	±	−
PAI-iiie	84	0.67	305	3.79	1.7	++	+	++	++	−	+	++	+	−
PAI-iiif	81	0.65	308	3.96	1.9	++	+	++	++	−	+	++	+	±

Solubility: ++, soluble at room temperature; +, soluble after heating; ±, partially soluble after heating; −, insoluble even on heating; DMAc: N,N-dimethylacetamide; DMSO: dimethyl sulfoxide; DMF: N,N-dimethylformamide; NMP: N-methyl pyrrolidone; THF: tetrahydrofuran; Py: pyridine; CF: chloroform.
[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30°C.
[b] Obtained in DMAc at a concentration of 0.1 mg/mL.
[c] Measured by GPC in DMF with polystyrene as a standard.
[d] Polymer was not soluble in DMAc.
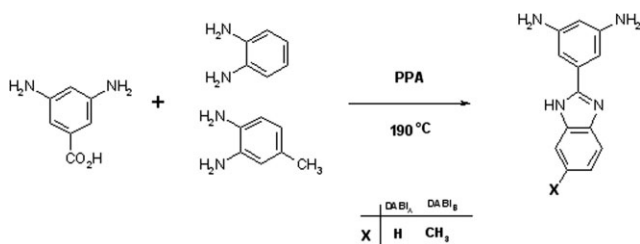
Scheme 1　Synthesis of DABI$_A$ and DABI$_B$ monomers.

weights were determined by gel permeation chromatography (GPC). GPC was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as the eluent. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were preformed on a Mettler TA4000 System under nitrogen atmosphere at heating rate of 10°C min^{-1}. Inherent viscosities (η_{inh}) of polymers were determined for solution of 0.5 g dL^{-1} in DMAc at 30°C using a Canon–Fenske viscometer. Elemental analyses were performed with a Perkin–Elmer model 2400 C, H, N analyzer. Mass spectroscopy data were recorded under electron impact at 70 eV on a Shimadzu GCMS-QP-1000 EX instrument.

RESULTS AND DISCUSSION

Monomer synthesis

The synthesis of diamine DABI$_A$ by several routes has been previously described. It was first prepared by Frost et al.[21] by a three-step route that involved the formation of a benzanilide intermediate and its conversion into the corresponding benzimidazole upon heating. Mikroyannidis[22] reported the synthesis of this monomer in three steps, with poly(phosphoric acid) (PPA) used to carry out the cyclodehydration

reaction, then this monomer was synthesized via a two-stage procedure that included the preparation of a dinitro intermediate, followed by its reduction into diamine.[20] In this investigation, DABI$_A$ and DABI$_B$ were prepared in one-step procedure by PPA in 190°C, which is outlined in Scheme 1. The reaction procedure is complicated due to the long experimental time and high-temperature reaction conditions. PPA is a relatively common solvent for preparing heterocyclic compounds by polycondensation.[23]

The diimide-dicarboxylic acid monomers DADI-i and DADI-ii containing pendent benzimidazole group and DADI-iii (as a reference) without pendent benzimidazole group were obtained according to the route illustrated in Scheme 2. They were prepared by the condensation of the appropriate diamine with two mole equivalents of trimellitic anhydride in refluxing glacial acetic acid. The condensation reaction between the amines and anhydride groups, as well as the subsequent cyclodehydration reaction was carried out in the heterogeneous solution. As example, the FTIR spectrum of DIDA-i exhibited characteristic absorptions at 2500–3480 (carboxylic acid O—H, N—H stretching), 1782 (symmetric imide C=O stretching), 1720 (asymmetric imide C=O stretching and acid C=O stretching), 1612 (C=N stretching), 1530 (N—H deformation) and 1350, 1087, and 725 cm^{-1} (imide ring deformation) confirming the presence of imide ring, benzimidazole segment, and carboxylic acid groups in the structures (Fig. 1).

The ^{1}H-NMR spectral data of the monomers are in the range of 7.22–8.44 ppm, which protons of the trimellitoyl groups revealed signals at downfield regions (around 8 ppm). The ^{13}C-NMR spectra exhibited 17 peaks for aromatic carbons of DIDA-i, 21 peaks for aromatic carbons of DIDA-ii, and 13 peaks peaks for aromatic carbons of DIDA-iii. Carbonyl carbons of carboxylic acid and imide groups resonate in the downfield region above 165 ppm. Figure 2 shows the ^{1}H-NMR and ^{13}C-NMR spectra of DIDA-i.
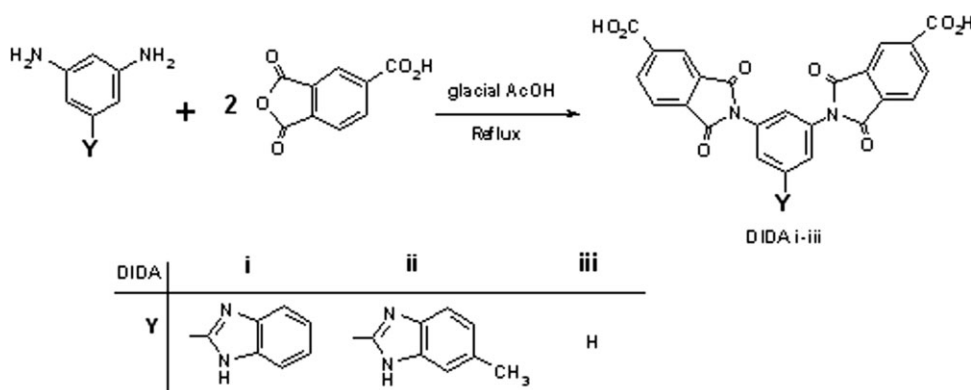
Scheme 2　Synthetic route used to obtain the imide-containing diacids (DIDA i-iii).
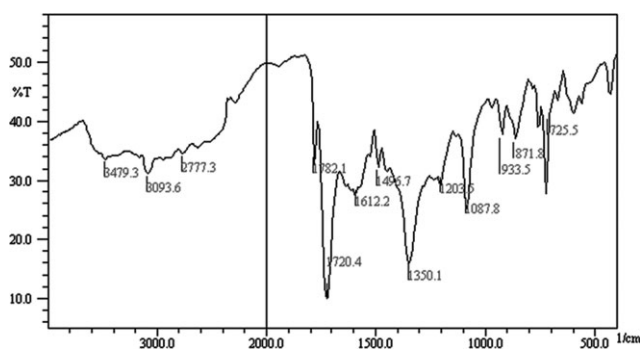
Figure 1 FTIR spectrum of DIDA-i.

Polymer synthesis

As shown in Scheme 3, two series of new PAI-(i, a–f) and PAI-(ii, a–f) were prepared from diimide-dicarboxylic acid DIDA-i and DIDA-ii with various aromatic diamines, a–f, by the direct condensation reaction by using by TPP/pyridine system as a condensing agent (Yamazaki process). For study of the pendant group effects, PAIs (iii, a–f) without the benzimidazole pendant group were also synthesized by a similar manner for comparison. The resulting PAIs possessed inherent viscosities ranging 0.46 and 0.81 dLg^{-1}, measured in DMAc at a concentration of 0.5 dL g^{-1} at 30°C. Inherent viscosities, weight-average molecular weights (M_w's), and polydispersities (M_w/M_n) of PAIs are summarized in Table II. Because, the inherent viscosity is a good criterion for the estimation of molecular weight the prepared PAIs showed reasonable molecular weights.

Behniafar reported that the ultraviolet maximum wavelengths (λ_{max}'s) of the polymers depending upon π to π* allowed transitions were also deter-mined and ranged between 292 and 319 nm. Generally, the highly conjugated aromatic structures of the obtained polymers lead to various absorption bands in their UV-Vis spectra, as a number of broad and sharp peak, which could be attributed to the various of allowed and forbidden electron transitions.[24]

Also, the structures of PAIs were confirmed by elemental analysis IR and ^{1}H-NMR spectral data. Representative FTIR spectrum of PAI-**iif** is shown in Figure 3. It displays characteristic absorption bands for the imide ring at around 1782 and 1728 cm^{-1}, which is indicative of the asymmetrical and symmetrical C=O stretching vibration, and at 1357, 1080, and 720 cm^{-1} due to imide ring deformation. The N—H stretching band of the amide and benz-imidazole groups could be observed around 3400–3300 cm^{-1}, and the C=O stretching band of amide group at 1670 cm^{-1}, the C=N stretching band benz-imidazole groups at 1612 cm^{-1} and the N—H bending and C—N stretching bands at 1550 cm^{-1} could also be observed. Other PAIs had similar functional groups. In general, the ^{1}H-NMR spectra of the resulting PAIs are divided three parts, with the first showing the imidazole-group protons in the most downfield region (around 12.50 ppm), the second the amide-group protons about 11, and third the aromatic protons in the region of about 6.61–8.57 ppm. On the basis of the description earlier, we can conclude that the PAIs have the expected structures.

Solubility behavior

The solubility of all PAIs was tested qualitatively in various organic solvents, with the results summarized in Table II. As expected, the bulky group
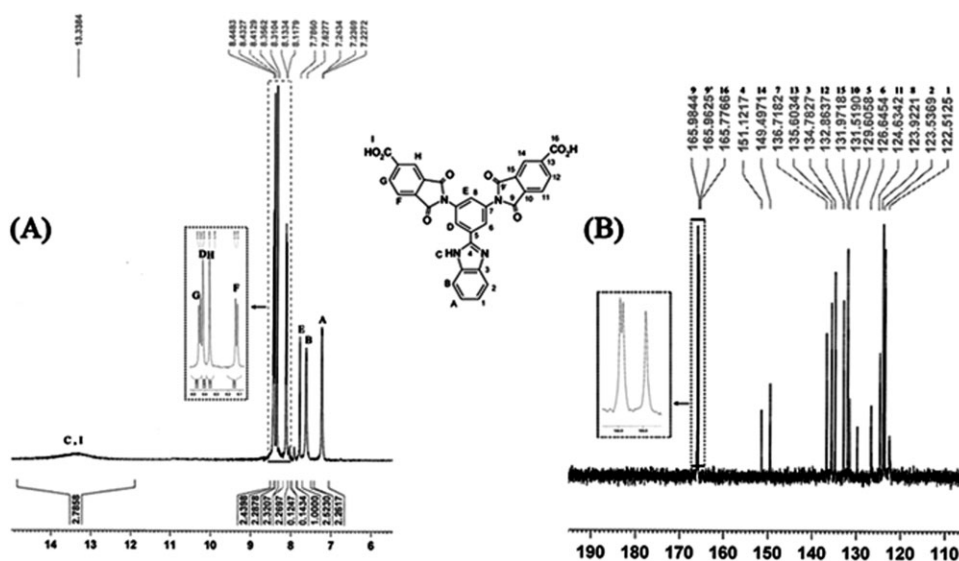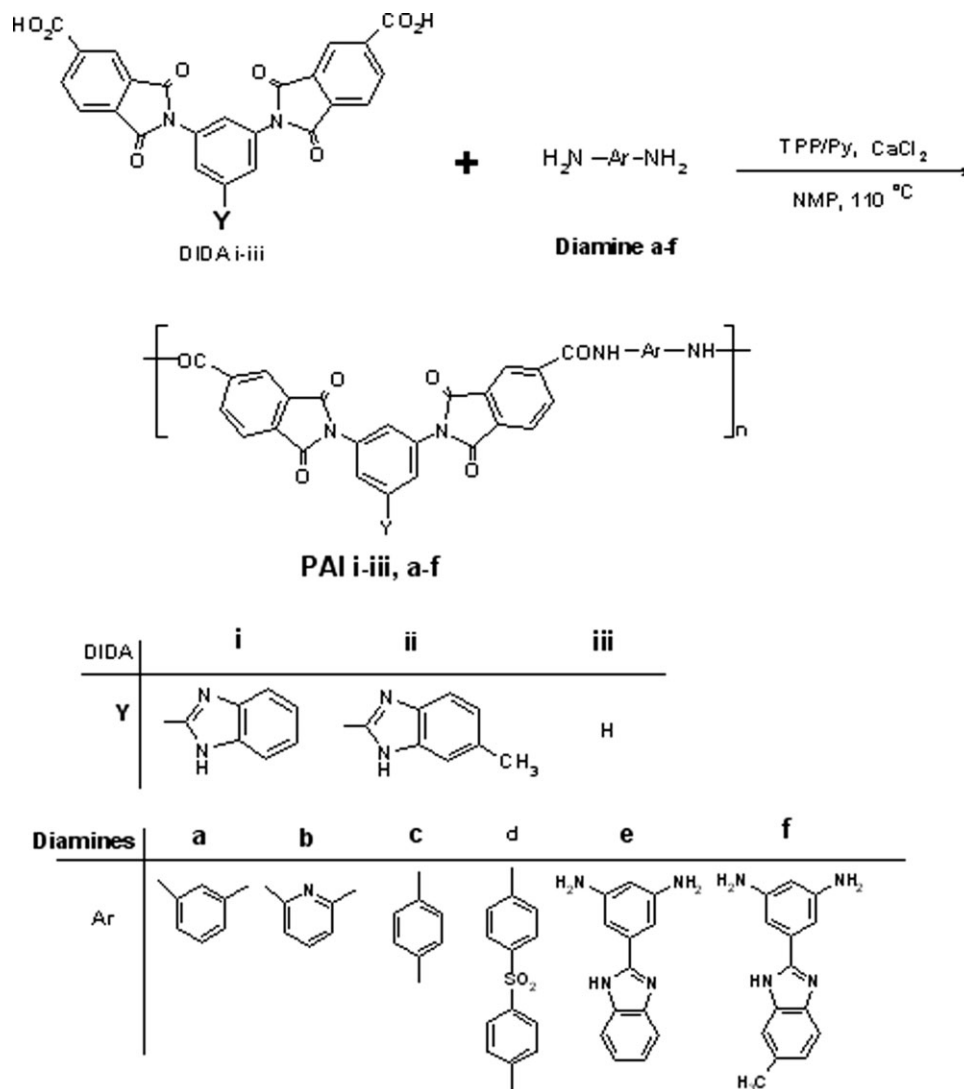

Figure 2 (A) ^{1}H-NMR and (B) ^{13}C-NMR spectra of DIDA-i in DMSO-d_6.

Scheme 3 Synthesis of poly(amide-imide)s.

improved the polymer solubility. All the polymers containing the benzimidazole pendent group were soluble at room temperature in polar solvents DMF, NMP, DMSO, DMAc, and H_2SO_4. Furthermore, factors related to diamine structure, such as *m-* or *p*-catenation, value of rigidity, bulky, and cranked structures have their effects on the solubility of the polymers. PAI-**ie**, **if**, **iie**, and **iif** were even somewhat soluble in less polar solvents such as *m*-cresol and pyridine owing to the presence of the bulky segments in their diamine moieties. The difference in solubility was attributed to the presence of bulky benzimidazole group, which hindered dense chain packing, thereby reducing the interchain interactions and enhancing solubility. Finally, from a comparison of the solubilities for the PAIs ia–f and PAIs iia–f, the PAIs containing 5-methyl benzimidazole units had not much better solubility than those of the PAIs containing benzimidazole units.

Thermal properties

Thermal properties of the resulting PAIs were determined by means of differential scanning calorimetry (DSC) as well as thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 10°C
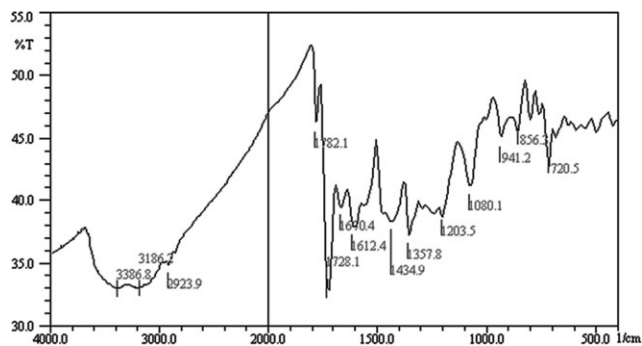

Figure 3 FT-IR spectrum of PAI-iif.

min^{-1} and the thermal data are summarized in Table III.

There is no melting endotherm present in the DSC thermograms, which is consistent with the amorphous nature of the PAIs. The glass-transition temperatures (T_g's), determined in second heating runs of DSC measurements, of the investigated PAIs were in the range of 385–334°C. Some structure–properties relations can be inferred from these data. The present of the benimidazole group on the T_g value could be appreciated when PAIs containing the pendent benzimidazole group [PAI-i(a–f)] and [PAI-ii(a–f)] were compared with PAIs without benzimidazole group [PAI-iii(a–f)] whereas the same type of structure was maintained. These reference PAIs showed lower T_g values than those having benzimidazole group, and this confirmed that the bulkiness and polarity of the benzimidazole group restricted the free rotation of the macromolecular chains leading to an enhanced T_g values.

The thermal stability was investigated by TGA with the T_d values (temperatures which correspond to a 10% weight loss) as a criterion of thermal stability. There was no significant difference in TGA curves of the PAIs. The new PAIs containing the benzimidazole group were more stable than the corresponding reference PAIs, displaying T_d values >528°C. For all polymers the residual weights at 800°C in nitrogen are still higher than 51%. For

Figure 4   TGA/DTG curves of PAI-ie.

example, the TGA/DTG thermogram of PAI-**ie** is presented in Figure 4.

CONCLUSIONS

Two new diimide-dicarboxylic acid monomers containing benzimidazole pendant group and a diimide-dicarboxylic acid monomer (as a reference) were successfully prepared and were used to synthesis a series of PAIs via Yamazaki's phosphorylation method using triphenyl phosphite and pyridine system. The results presented herein also demonstrate clearly that incorporating the benzimidazole pendant group into the polymer backbone remarkably enhanced the solubility and thermal stability of the polymers. Thus, they are considered to be new promising processable high-temperature polymeric materials.

TABLE III
Thermal Properties of the PAIs

code	$T_g{}^a$ (°C)	$T_d{}^b$ (°C)	Char Yield^c (wt %)
PAI-ia	364	541	61
PAI-ib	365	552	58
PAI-ic	–^{d}	563	58
PAI-id	371	555	53
PAI-ie	385	568	63
PAI-if	372	561	57
PAI-iia	351	531	59
PAI-iib	345	535	58
PAI-iic	352	557	57
PAI-iid	362	543	52
PAI-iie	373	558	58
PAI-iif	354	544	52
PAI-iiia	334	528	51
PAI-iiib	339	531	55
PAI-iiic	341	533	56
PAI-iiid	342	536	57
PAI-iiie	361	541	59
PAI-iiif	353	532	53

^{a} Form the second heating traces of DSC measurements with a heating rate of 10°C/min in nitrogen.
^{b} Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min in nitrogen.
^{c} Residual wt % at 800°C under a nitrogen atmosphere.
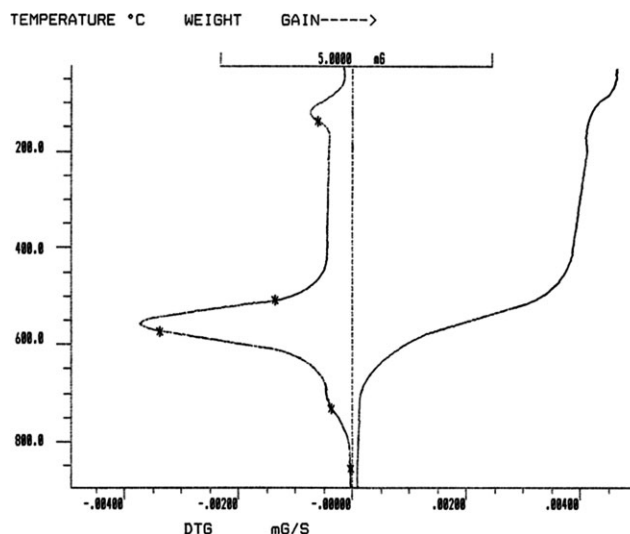^{d} No discernible transition was observed on the DSC traces.

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