Modified Poly(ether–imide–amide)s with Pendent Benzazole Structures: Synthesis and Characterization

Hojjat Toiserkani[1,2]

[1]*Department of Chemistry, College of Science, Hormozgan University, Bandar Abbas 3995, Iran*
[2]*College of Oil Engineering, Hormozgan University, Bandar Abbas 3995, Iran*

ABSTRACT: Three series of novel modified poly(ether–imide–amide)s (PEIAs) having pendent benzazole units were prepared from diimide–dicarboxylic acids, including 2-[3,5-bis(4-trimellitimidophenoxy) phenyl]benzimidazole, 2-[3,5-bis(4-trimellitimidophenoxy) phenyl]benzoxazole, and 2-[3,5-bis(4-trimellitimidophenoxy) phenyl]benzothiazole, with various diamines by direct polycondensation in N-methyl-2-pyrrolidone with triphenyl phosphite and pyridine as condensing agents. These new diimide–dicarboxylic acids containing ether linkages and benzazole pendent groups were synthesized by the condensation reaction of 5-(2-benzimidazole)-1,3-bis(4-aminophenoxy)benzene, 5-(2-benzoxazole)-1,3-bis(4-aminophenoxy)benzene, or 5-(2-benzothiazole)-1,3-bis(4-aminophenoxy)benzene with trimellitic anhydride, respectively. All of the polymers were obtained in quantitative yields with inherent viscosities of 0.39–0.65 dL/g. For comparative purposes, the corresponding unsubstituted PEIAs were also prepared by the reaction of a diimide–dicarboxylic acid monomer lacking benzazole pendent groups, namely, 3,5-bis(4-trimellitimidophenoxy) phenyl, with the same diamines under similar conditions. The solubilities of the modified PEIAs in common organic solvents and their thermal stability were enhanced compared to those of the corresponding unmodified PEIAs. The glass-transition temperature, 10% weight loss temperature, and char yields at 800°C were 19–31°C, 22–57°C and 4–8% higher, respectively, than those of the unmodified polymers. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1576–1585, 2012

Key words: high performance polymers; modification; thermal properties

INTRODUCTION

Among the various heterocyclic polymers investigated for high-performance applications, aromatic polyimides are used widely in the semiconductor and electronic packaging industries because of their outstanding thermal stability, good insulation properties with a low dielectric constant, good adhesion to common substrates, and superior chemical stability.[1,2] Despite their widespread use, polyimides are generally intractable and lack the properties essential for successful fabrication into useful forms because of their high melting temperature or glass-transition temperature (T_g) and their limited solubility in organic solvents. Therefore, the incorporation of new functionalities to make polyimides more tractable without deteriorating their own excellent properties has become one important target of polyimide chemistry.[3–5] One of the important modifications for making processable polyimides is copolymerization. The replacement of polyimides by copolyimides such as poly(amide–imide)s (PAIs) may be useful in the modification of the intractable nature of polyimides. PAIs contain both amide and cyclic imide units along the polymer chain and, hence, constitute a polymer class with average properties between aromatic polyamides and polyimides. They possess good thermal properties compared to polyamides and better melt processability than polyimides. In addition, the synthetic approach to PAIs presents the option of introducing specific segments between amide and imide groups.[6] The incorporation of ether groups or other flexible linkages into the main chain generally leads to lower T_g and a significant improvement in solubility without a great sacrifice of other advantageous polymer properties. On the other hand, the introduction of bulky groups into the rigid polymer chain can impart a significant increase in T_g through the restriction of the segmental mobility and provide an enhanced solubility due to decreasing packing and crystallinity.[7–10] If the pendent groups are carefully chosen, it is possible for one to promote solubility without impairing the thermal and mechanical properties to any great extent. The combination of these two structural modifications minimized the trade-off between the processability and useful/positive properties, such as the solubility of aromatic PAIs.[11–24]

In previous work, we reported the synthesis and characterization of modified PAIs bearing benzazole

Correspondence to: H. Toiserkani (toiserkani@yahoo.com).

pendent groups with better solubility and thermally stability than the corresponding unsubstituted PAIs.[25,26] It is important to note that when heterocyclic rings, such as benzimidazole, benzoxazole, or benzothiazole, were used as pendent groups, beneficial effects were observed, not only in the solubility but also in the thermal properties, because benzimidazole, benzoxazole, and benzothiazole are among the most heat-resistant structures.[27] In this study, three new benzazole-based and imide-ring-containing dicarboxylic acid bearing flexible ether linkages, including 2-[3,5-bis(4-trimellitimidophenoxy) phenyl]benzimidazole (**1**), 2-[3,5-bis(4-trimellitimidophenoxy) phenyl]benzoxazole (**2**), and 2-[3,5-bis(4-trimellitimidophenoxy) phenyl]benzothiazole (**3**), were synthesized and used to prepare new modified poly(amide–ether–imide)s by their polycondensation with aromatic diamines. The effect of benzazole pendent groups on the solubility and thermal properties of the modified poly(ether–imide–amide)s (PEIAs) was investigated by comparison with PEIAs without benzazole pendent groups (reference PEIAs), obtained from 3,5-bis(4-trimellitimidophenoxy) phenyl (**4**) and the same diamines.

EXPERIMENTAL

Materials

Trimellitic anhydride (>97% purity, Merck, Darmstadt, Germany) and triphenyl phosphite (TPP; 97% purity, Sigma-Aldrich, Shanghai, China) were used as received without further purification. N-Methyl-2-pyrrolidone (NMP) was distilled over CaH_2, and pyridine (Py) was dried in KOH pellets and stored over 4-Å molecular sieves. Commercially obtained calcium chloride was dried in vacuo at 180–200°C for 8 h before each run. 1,3-Phenylenediamine (**a**; Merck) was purified by sublimation before use. Aromatic diamines, including 5-(2-benzoxazole)-1,3-phenylenediamine (**b**; mp = 226–230°C),[26] 5-(2-benzothiazole)-1,3-phenylenediamine (**c**; mp = 167–171°C),[26] 5-(2-benzimidazole)-1,3-bis(4-aminophenoxy) benzene (mp = 218–222°C),[28] 5-(2-benzoxazole)-1,3-bis(4-aminophenoxy)benzene (mp = 168–171°C),[28] and 5-(2-benzothiazole)-1,3-bis(4-aminophenoxy)benzene (mp = 162–165°C),[28] were synthesized according to our previous works. 1,3-Bis(4-aminophenoxy)benzene (**6**; mp 114–116°C) was prepared by the nucleophilic substitution reaction of the corresponding bisphenol precursor, resorcinol, and 4-fluoronitrobenzene in the presence of potassium carbonate, followed by hydrazine catalytic reduction of the intermediate dinitro compound. Glacial acetic acid (purity > 99%) was purchased from Merck and was used without further purification.

Measurements

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AV-500 FT NMR spectrometer (Germany) in hexadeuterated dimethyl sulfoxide (DMSO-d_6) at 25°C with frequencies of 500.13 and 125.77 MHz for the ^{1}H and ^{13}C spectra, respectively. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor-27 spectrometer for the measurement of infrared absorption spectra for the monomers and polymers. The spectra of solids were obtained with KBr pellets. The melting points were determined with a Buchi 535 melting-point apparatus (Switzerland). Thermogravimetric analysis (TGA) was conducted with a DuPont 2000 thermal analyzer (USA) under a nitrogen atmosphere (20 cm^3/min) at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) was recorded on a PerkinElmer Pyris 6 DSC instrument (USA) under a nitrogen atmosphere (20 cm^3/min) at a heating rate of 20°C/min. The inherent viscosities (η_{inh}'s) of the polymers were determined for a solution of 0.5 g/dL in N,N-dimethylacetamide (DMAc) at 30°C with a Canon-Fenske viscometer. Elemental analyses were performed with a PerkinElmer 2400 CHN elemental analyzer (USA). Mass spectroscopy data were recorded under electron impact at 70 eV on a Shimadzu GCMS-QP 1000 EX instrument (Japan).

2-[3,5-bis(4-trimellitimidophenoxy)-phenyl]benzimidazole (1)

To a 100-mL, round-bottom flask fitted with a magnetic stirrer and a reflux condenser were added 4.08 g (0.01 mol) of 5-(2-benzimidazole)-1,3-bis(4-aminophenoxy)benzene, 4.61 g (0.024 mol) of trimellitic anhydride, and 45 mL of 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, then purified by recrystallization from N,N-dimethylformamide (DMF), and dried in vacuo at 100°C for 12 h to afford 6.58 g (87%) of **1** as a yellow–brown solid (mp > 300°C).

The other monomers, **2** (yield = 84%; mp > 300°C), **3** (yield = 90%; mp > 300°C), and **4** (a reference, yield = 96%; mp > 300°C), were synthesized with the same procedure as that used for **1** from 5-(2-benzoxazole)-1,3-bis(4-aminophenoxy)benzene, 5-(2-benzothiazole)-1,3-bis(4-aminophenoxy)benzene, and **6**, respectively, instead of 5-(2-benzimidazole)-1,3-bis(4-aminophenoxy)benzene. The spectral data for these monomers are shown in Table I.

Preparation of the PEIAs

A typical synthetic procedure of the PEIAs was as follows: a mixture of 0.491 g (0.650 mmol) of **1** and

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

Code	Spectral data
1	^{1}H-NMR (DMSO-d_6, δ, ppm): 13.34 (br, COOH and N—H imidazole), 8.41 (d, ^3J = 7.8 Hz, 2H), 8.29 (s, 2H), 8.07 (d, ^3J = 7.8 Hz, 2H), 7.71 (d, ^4J = 1.9 Hz, 2H), 7.58 (m, 2H), 7.54 (d, ^3J = 8.7 Hz, 4H), 7.33 (d, ^3J = 8.7 Hz, 4H), 7.19 (m, 2H), 6.98 (s, 1H). ^{13}C-NMR (DMSO-d_6, δ, ppm): 166.26, 165.75, 158.19, 155.72, 149.71, 136.61, 135.38, 134.78, 133.27, 131.97, 129.10, 127.40, 126.21, 123.68, 123.30, 122.10, 121.96, 119.09, 111.65, 111.13. FTIR (KBr, cm^{-1}): 3340–2500 (m, br), 1781 (m, sh), 1719 (s, sh), 1689 (m, sh), 1612 (m, sh), 1595 (m, sh), 1506 (s, sh), 1465 (w, sh), 1383 (s, sh), 1224 (s, sh), 1170 (m, sh), 1094 (m, sh), 997 (m, sh), 887 (w, sh), 784 (w, sh), 728 (m, sh). m/z: 756 [M$^+$]. ANAL. Calculated for C$_{43}$H$_{24}$N$_4$O$_{10}$: C, 68.25%; H, 3.20%; N, 7.40%. Found: C, 68.17%; H, 3.23%; N, 7.45%.
2	^{1}H-NMR (DMSO-d_6, δ, ppm): 13.54 (br, COOH), 8.41 (d, ^3J = 8.1 Hz, 2H), 8.30 (s, 2H), 8.07 (d, ^3J = 8.1 Hz, 2H), 7.81 (m, 2H), 7.56 (d, ^3J = 8.8 Hz, 4H), 7.54 (d, ^4J = 2.3 Hz, 2H), 7.41 (m, 2H), 7.37 (d, ^3J = 8.8 Hz, 4H), 7.12 (t, ^4J = 2.3 Hz, 1H). ^{13}C-NMR (DMSO-d_6, δ, ppm): 166.37, 165.93, 160.89, 158.83, 155.09, 150.24, 141.18, 137.38, 135.42, 134.63, 131.98, 129.27, 127.95, 125.99, 125.10, 123.71, 123.36, 120.12, 119.80, 119.31, 112.44, 111.27, 111.15. IR (KBr, cm^{-1}): 3450–2600 (m, br), 1781 (m, sh), 1721 (s, sh), 1693 (w, sh), 1631 (m, sh), 1591 (m, sh), 1553 (w, sh), 1507 (s, sh), 1434 (w, sh), 1385 (m, sh), 1291 (w, sh), 1224 (s, sh), 1170 (m, sh), 1093 (m, sh), 1001 (w, sh), 947 (w, sh), 885 (w, sh), 728 (m, sh). m/z: 757 [M$^+$]. ANAL. Calculated for C$_{43}$H$_{23}$N$_3$O$_{11}$: C, 68.17%; H, 3.06%; N, 5.55%. Found: C, 68.06%; H, 3.11%; N, 5.67%.
3	^{1}H-NMR (DMSO-d_6, δ, ppm): 13.39 (br, COOH), 8.38 (d, ^3J = 8.1 Hz, 2H), 8.27 (s, 2H), 8.13 (d, ^3J = 7.8 Hz, 1H), 8.06 (dd, ^3J = 8.0 Hz, ^3J = 7.8 Hz, 3H), 7.58 (d, ^3J = 8.8 Hz, 4H), 7.52 (t, ^3J = 7.3 Hz, 1H), 7.49 (d, ^4J = 2.1 Hz, 2H), 7.45 (t, ^3J = 7.3 Hz, 1H), 7.34 (d, ^3J = 8.8 Hz, 4H), 6.99 (t, ^4J = 2.2 Hz, 1H). ^{13}C-NMR (DMSO-d_6, δ, ppm): 166.25, 165.77, 165.64, 158.62, 155.29, 153.27, 136.48, 135.86, 135.44, 134.84, 134.56, 131.99, 129.17, 127.73, 128.81, 125.90, 123.75, 123.35, 123.20, 122.41, 119.52, 114.95, 111.75. FTIR (KBr, cm^{-1}): 3400–2500 (m, br), 1771 (m, sh), 1721 (s, sh), 1694 (w, sh), 1632 (m, sh), 1591 (w, sh), 1506 (s, sh), 1477 (m, sh), 1389 (s, sh), 1229 (s, sh), 1167 (m, sh), 1108 (m, sh), 965 (m, sh), 841 (w, sh), 790 (w, sh), 730 (m, sh). m/z: 773 [M$^+$]. ANAL. Calculated for C$_{43}$H$_{23}$N$_3$O$_{10}$S: C, 66.75%; H, 3.00%; N, 5.43%. Found: C, 66.69%; H, 3.03%; N, 5.50%.
4	^{1}H-NMR (DMSO-d_6, δ, ppm): 13.72 (br, COOH), 8.39 (d, ^3J = 7.7 Hz, 2H), 8.26 (s, 2H), 8.04 (d, ^3J = 7.7 Hz, 2H), 7.49 (d, ^3J = 8.8 Hz, 4H), 7.45 (t, ^3J = 8.2 Hz, 1H), 7.23 (d, ^3J = 8.8 Hz, 4H), 6.87 (dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz, 2H), 6.80 (t, ^4J = 2.1 Hz, 1H). ^{13}C-NMR (DMSO-d_6, δ, ppm): 166.24, 165.74, 157.75, 155.91, 136.47, 135.40, 134.82, 131.98, 131.34, 129.01, 127.16, 123.70, 123.33, 118.96, 113.98, 109.67. FTIR (KBr, cm^{-1}): 3459–2650 (m, br), 1781 (m, sh), 1719 (s, sh), 1587 (m, sh), 1506 (s, sh), 1431 (w, sh), 1398 (m, sh), 1226 (s, sh), 1170 (m, sh), 1121 (m, sh), 1093 (m, sh), 998 (w, sh), 937 (w, sh), 832 (w, sh), 777 (w, sh), 727 (m, sh). m/z: 640 [M$^+$]. ANAL. Calculated for C$_{36}$H$_{20}$N$_2$O$_{10}$: C, 67.50%; H, 3.15%; N, 4.37%. Found: C, 67.34%; H, 3.20%; N, 4.40%.

2.5 mL of NMP was stirred under nitrogen atmosphere and heated to 70°C to dissolve **1**. Py (0.6 mL), TPP (0.7 mL), and calcium chloride (0.25 g) 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, 0.650 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 the solution was allowed to stir for an additional 5 min. After the completion of polymerization, the viscous mixture was poured into methanol. The precipitated polymer was filtered, washed thoroughly with methanol and hot water, and then dried under a vacuum to give 0.495 g (92%) of PEIA1a. The η$_{inh}$ of polymer PEIA1a was 0.51 dL/g at a concentration of 0.5 g/dL in DMAc at 30°C.

ANAL. Calcd for C$_{49}$H$_{28}$N$_6$O$_8$ (828.8)$_n$: C, 71.01%; H, 3.40%; N, 10.14%. Found: C, 70.82%; H, 3.48%; N, 10.32%.

The other PEIAs were synthesized by a procedure analogous to that described previously.

The η$_{inh}$ values and yields of PEIAs are summarized in Table II. The spectroscopic data for the PEIAs are discussed in the Results and Discussion section.

RESULTS AND DISCUSSION

Synthesis processes

The reaction between aromatic diamines and trimellitic anhydride is the usual manner to prepare imide-ring-containing aromatic dicarboxylic acids. This route is widely used in the field of polymeric materials for the synthesis of some copolyimides, including PAIs[24,25] and poly(ester–imide)s.[29–31] According to this strategy, bis(ether–amine)s, such as 5-(2-benzimidazole)-1,3-bis(4-aminophenoxy)benzene, 5-(2-benzoxazole)-1,3-bis(4-aminophenoxy)benzene, 5-(2-benzothiazole)-1,3-bis(4-aminophenoxy)benzene, and **6** were reacted with 2 mol equiv of trimellitic anhydride in refluxing glacial acetic acid to obtain **1, 2, 3,** and **4**, respectively. The addition reaction between the amino and anhydride groups and the subsequent thermal cyclodehydration reaction was carried out in a pale yellow heterogeneous solution. Scheme 1 shows the reaction route for the synthesis of monomers **1, 2, 3,** and **4**. The chemical structures of all of these new monomers were confirmed by means of elemental analysis and mass, FTIR, and NMR spectroscopy. As shown in Figure 1, the FTIR spectra of all of the monomers showed absorption bands around 2500–3450 cm^{-1} [C(O)O—H], about 1780 cm^{-1} (symmetric imide C=O stretching), about

TABLE II
Structures, Yields, and η_{inh} Values of the PEIAs

Polymer code	Polymer structure	Yield (%)	η_{inh} (dL/g)[a]	Polymer code	Polymer structure	Yield (%)	η_{inh} (dL/g)[a]
PEIA1a		92	0.51	PEIA3a		86	0.62
PEIA1b		88	0.47	PEIA3b		90	0.52
PEIA1c		84	0.39	PEIA3c		87	0.49
PEIA2a		91	0.60	PEIA4a		94	0.65
PEIA2b		91	0.48	PEIA4b		91	0.61
PEIA2c		87	0.45	PEIA4c		91	0.53

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30°C.

1720 cm^{-1} (asymmetric imide C=O stretching), about 1690 cm^{-1} (acid C=O stretching), about 1612–1630 cm^{-1} (C=N stretching), about 1380, 1080, and 725 cm^{-1} (imide ring deformation), and about 1220 cm^{-1} (C—O—C stretching); these confirmed the presence of imide rings, carboxylic acid groups, benzazole segments, and ether linkages in their structures. Figure 2 shows the ^{1}H-NMR spectra of all four

diimide–dicarboxylic acid monomers. The ^{1}H-NMR spectral data of the monomers showed aromatic protons in the range 6.80–8.41 ppm with expected multiples and integration; the protons of the trimellitoyl groups revealed signals at downfield regions (ca. 8 ppm). The strong electron-withdrawing effect of the benzazole pendent group was clearly observed from the chemical shifts of the g protons and was still
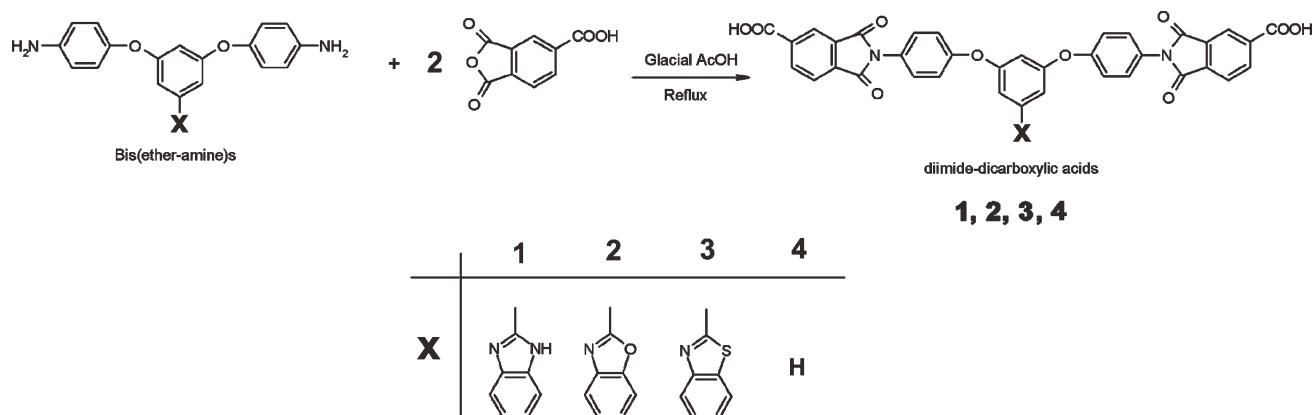
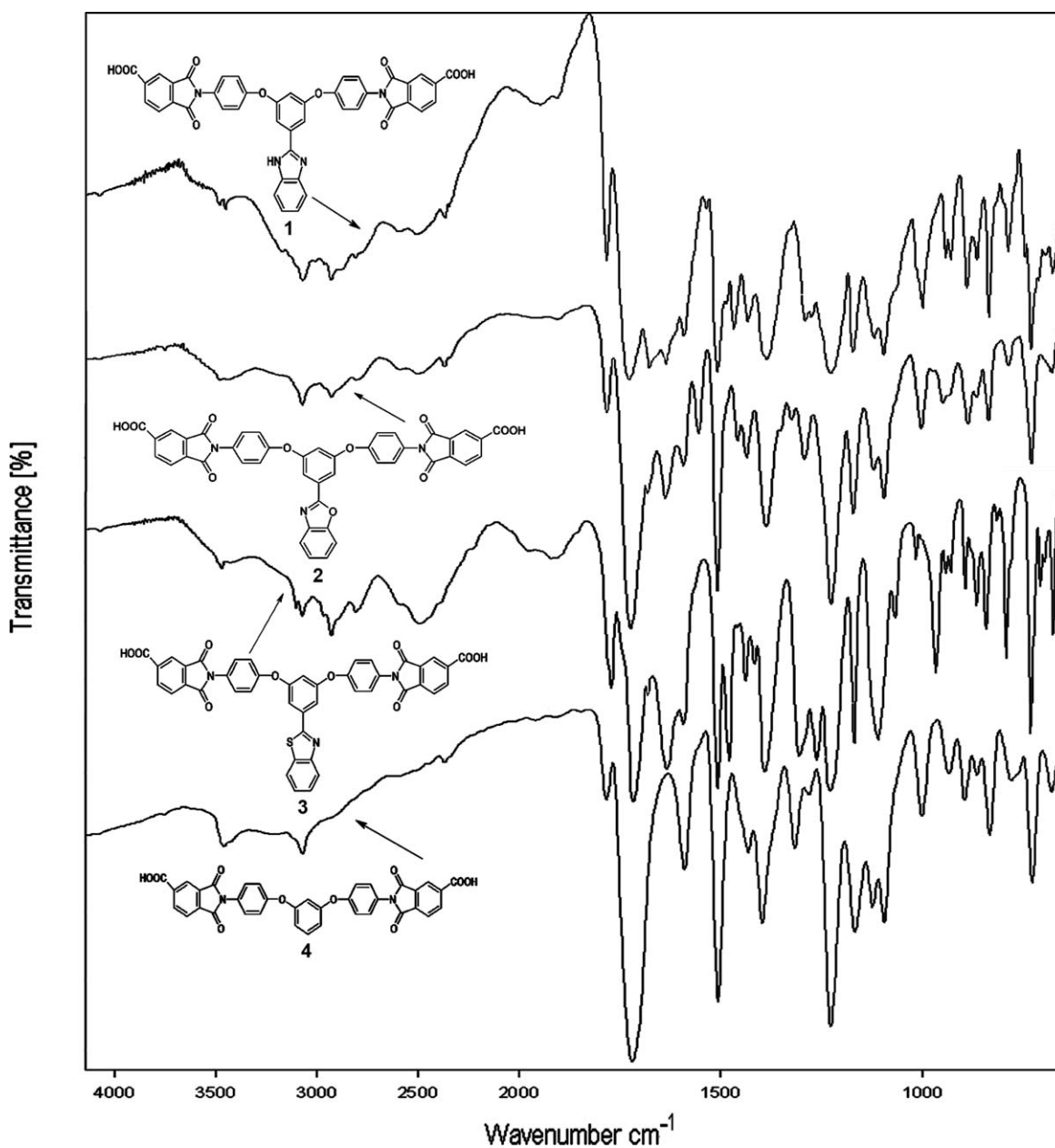
Scheme 1 Synthesis procedure of monomer **1**.

Figure 1 FTIR spectra of all of the monomers.

more noticeable from the h protons. A comparison with the spectrum of **4** (as a reference) without pendent groups showed downfield shifts of 0.18 and 0.83 ppm for the benzimidazole group (**1**), 0.33 and 0.66 ppm for benzoxazole groups (**2**), and 0.19 and 0.62 ppm for benzothiazole groups (**3**) for g and h protons. The ^{13}C-NMR spectra exhibited 20 different peaks for the aromatic carbons of **1**, 23 different peaks for aromatic carbons of **2** and **3**, and 16 different peaks for the aromatic carbons of **4**. The carbonyl carbons of carboxylic acid and imide groups resonated in the downfield region above 165 ppm.

The phosphorylation method as a direct polyamidation involves the one-pot polycondensation of aro-matic dicarboxylic acids with aromatic diamines in the presence of an aryl phosphite, such as TPP, and an organic base, such as Py. The addition of inorganic salts, such as $CaCl_2$, improves the solubility of the polymer and the maximum attainable molecular weights.[32] In this study, the mentioned method was used to prepare wholly aromatic PEIAs. All of the reactions proceeded smoothly in homogeneous solutions with high yields up to 84%. Scheme 2 shows the reaction route used to obtain these benzazole-con-taining PEIAs. To study the pendent group effects, PEAI4a–PEAI4c references without the pendent groups were also synthesized by a similar manner for comparison. Some characteristics of the resulting
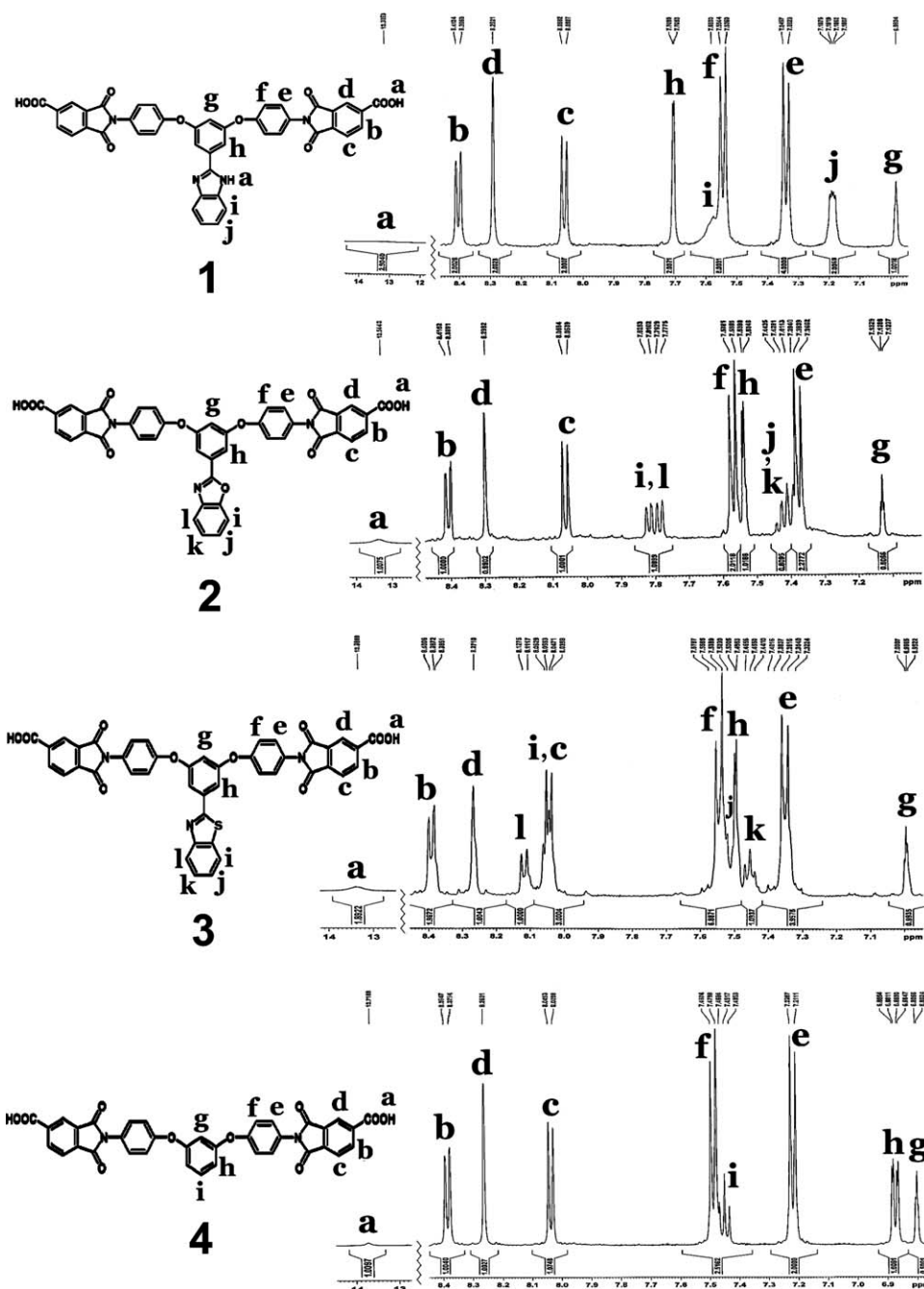
Figure 2 ^{1}H-NMR spectra of the diimide–dicarboxylic acid monomers (500 MHz, DMSO-d_6).

PEIAs, including η_{inh}, were measured in DMAc at a concentration of 0.5 dL/g at 30°C, and the yields of the resulting polymers are tabulated in Table II.

The synthesized polymers were characterized by their FTIR and ^{1}H-NMR spectra. The FTIR spectra of the PEIAs showed characteristic absorptions for the imide ring around 1780 and 1728 cm^{-1} (imide I), indicative of the asymmetrical and symmetrical C=O stretching vibration, and at 1370 cm^{-1} (imide II), 1080 cm^{-1} (imide III), and 725 cm^{-1} (imide IV), whereas the imide I, III, and IV bands were assigned to axial, transverse, and out-of-plane vibrations,

respectively, of the cyclic imide structure. The N—H stretching band of the amide were observed around 3440 cm^{-1}, and the C=O stretching band of amide group was observed at 1670 cm^{-1}. The C=N stretching bands of the benzimidazole, benzoxazole, or benzothiazole groups at 1612–1633 cm^{-1} and the N—H bending and C—N stretching bands at 1550 cm^{-1} were also observed. Figure 3 shows typical FTIR [Fig. 3(A)] and ^{1}H-NMR [Fig. 3(B)] spectra of PEAI3b. On the basis of the previous description, we concluded that the PEIAs had the expected structures.
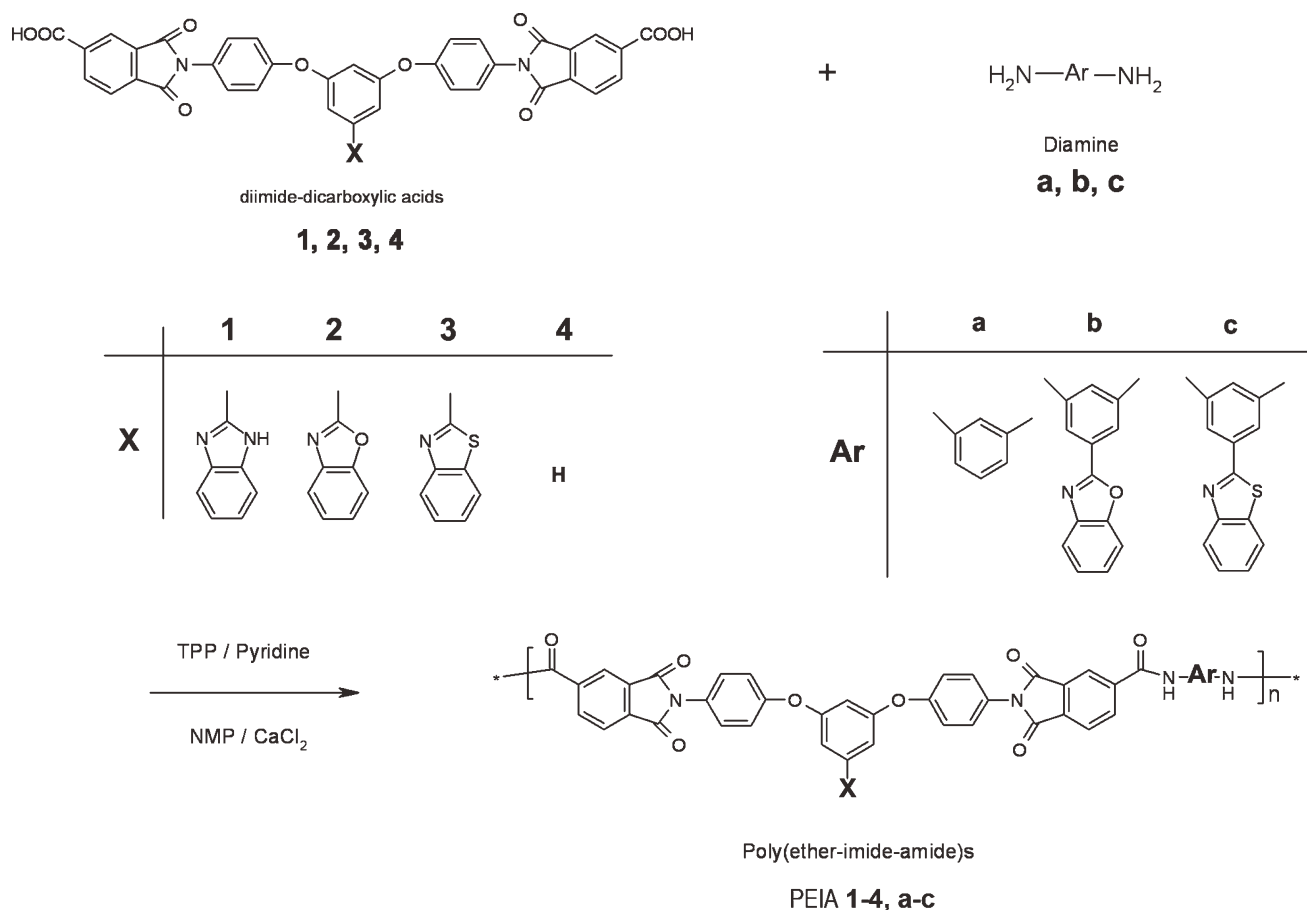
Scheme 2 Synthesis of the modified and reference PEIAs.

Properties of the PEIAs

The organosolubility behavior of all of the PEIAs was tested qualitatively in various organic solvents, with the results summarized in Table III. One of the aims of this investigation was the enhancement of the polymer solubility by the introduction of voluminous pendent groups along the polymer backbone. Almost all of the modified PEIAs were soluble in polar aprotic solvents [DMF, NMP, DMAc, and dimethyl sulfoxide (DMSO)] and concentrated H_2SO_4 at room temperature or upon heating. They also showed moderate solubilities in m-cresol and Py, whereas they were partially soluble in chloroform (CF) and tetrahydrofuran (THF). Modified PEIAs, PEAI1a–PEAI1c, PEAI2a–PEAI2c, and PEAI3a–PEAI3c displayed almost the same solubility in these solvents. Moreover, the modified PEIAs prepared herein were more soluble in less polar solvents, such as m-cresol, Py, CF, and THF, than those of the analogous PAIs reported in our previous articles.[23,24] In contrast, the unmodified PEIAs (reference PEAIs, PEAI4a–PEAI4c) dissolved at ambient temperature only in concentrated H_2SO_4 and upon heating in polar aprotic solvents. In addition, they were completely insoluble in less efficient solvents, such as m-cresol, Py, CF, and

THF. In general, the modified PEIAs displayed an increased solubility in comparison with the unmodified series. This was attributable in part to the packing-disruptive structure of the diimide–dicarboxylic acid components; this resulted in a high steric hindrance for close-chain packing and, thus, reduced interchain interactions. The chain separation effect accounted for a weakening of the strong interactions through hydrogen bonding, and the steric factor must have been dominant because the other effects, such as dipole attraction or chain rigidity enhancement, should have worked against good solubility.

TGA and DSC were used to evaluate the thermal properties of the PEIAs, and the results, including T_g values and the temperature at 10% weight loss (T_{10}) in nitrogen, and the anaerobic char yield at 800°C for all polymers are summarized in Table IV. The thermal stability was investigated by TGA with the T_{10} values as a criterion of thermal stability. There was no significant difference in the TGA curves of the PEIAs. The modified polymers started to lose weight at higher temperatures than the corresponding unmodified ones because their T_{10} values were higher by 22–57°C. In addition, the modification of polymers increased their anaerobic char
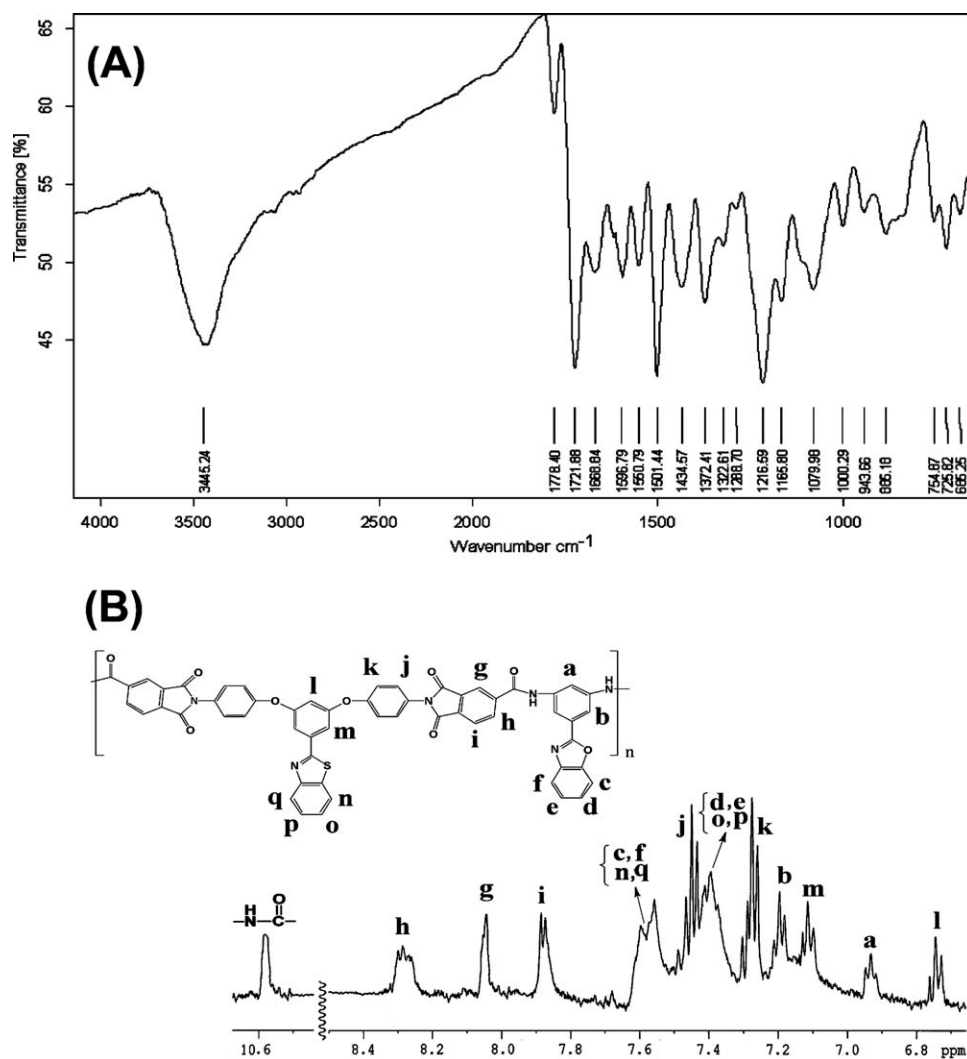
Figure 3   (A) FTIR and (B) ^{1}H-NMR spectra of PEAI3b (500 MHz, DMSO-d_6).

TABLE III
Solubility of the PEIAs

Polymer code	Solvent[a]								
	DMAc	DMSO	DMF	NMP	*m*-cresol	THF	Py	CF	H$_2$SO$_4$
PEIA1a	+h	+h	+h	+h	±	−	−	−	+
PEIA1b	+	+h	+	+	±	±	±	−	+
PEIA1c	+	+	+	+	+h	±	+h	±	+
PEIA2a	+h	+h	+h	+h	±	±	−	−	+
PEIA2b	+	+	+	+	+h	±	+h	±	+
PEIA2c	+	+	+	+	+h	±	+h	±	+
PEIA3a	+h	+h	+h	+h	±	−	−	−	+
PEIA3b	+	+	+h	+	+h	±	+h	±	+
PEIA3c	+	+h	+	+	+h	±	+h	±	+
PEIA4a	±	±	+h	+h	−	−	−	−	+
PEIA4b	+h	±	+h	+h	−	−	−	−	+
PEIA4c	+h	+h	+h	+h	−	−	−	−	+

[a] Qualitative solubility was determined by the dissolution of 10 mg of PEIAs in 1 mL of solvent at room temperature or upon heating. +, soluble at room temperature; +h, soluble on heating; ±, partially soluble on heating; −, insoluble even on heating.

TABLE IV
Thermal Properties of the PEIAs

Polymer code	T_g (°C)[a]	T_{10} (°C)[b]	Char yield (wt %)[c]
PEIA1a	256	501	49
PEIA1b	267	523	58
PEIA1c	272	531	57
PEIA2a	263	513	52
PEIA2b	288	541	61
PEIA2c	283	535	55
PEIA3a	262	510	50
PEIA3b	277	534	58
PEIA3c	282	527	58
PEIA4a	232	456	44
PEIA4b	262	514	55
PEIA4c	264	513	54

[a] From the second heating traces of DSC measurements with a heating rate of 20°C/min in nitrogen.
[b] Recorded by TGA at a heating rate of 20°C/min in nitrogen.
[c] Char yield at 800°C.

yield at 800°C by 4–8%. The heat-resistant benzimidazole, benzoxazole, and benzothiazole structure incorporated as a pendent group to the polymer backbone was responsible for this behavior. Upon comparing the chemical structures of the pendent groups, we observed that benzoxazole and benzothiazole showed better thermal stability than benzimidazole. DSC experiments were carried out at a heating rate of 20°C/min in nitrogen. Rapid cooling from 350°C to room temperature produced predominantly amorphous samples, so the T_g's of all of the polymers were easily read in the subsequent heating traces. A representative DSC curve of the polymer PEIA1b is also illustrated in Figure 4. The values of T_g listed in Table IV confirmed that the introduction of pendent benzimidazole, benzoxazole, or benzothiazole rings caused increases between 19 and 31°C in the T_g values compared with the unmodified PEIAs; this supported the preliminary assumption regarding the beneficial effect of the pendent heterocycles on the thermal transi-
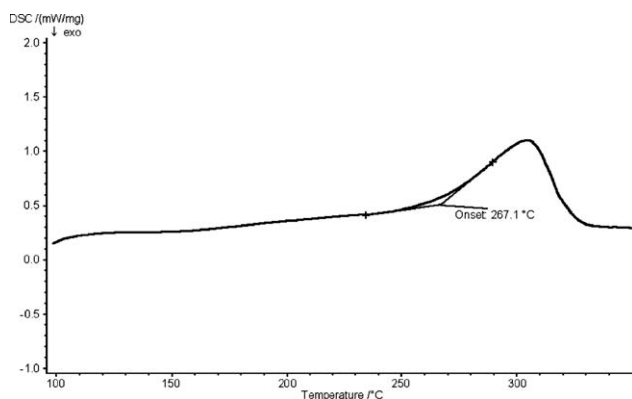
tions of aromatic PEIAs. In addition, the modified PEIAs displayed higher T_g values than the reference polymers; this may have been due to the fact that the benzazole ring on the phenylene unit inhibited the free rotation of the polymer chains and led to an enhanced T_g value.

CONCLUSIONS

Three novel benzimidazole, benzoxazole, and benzothiazole-containing diimide–dicarboxylic acid monomers, **1**, **2**, and **3**, and a diimide–dicarboxylic acid monomer, **4** (a reference), were successfully prepared and used to synthesis a series of PEIAs via direct polyamidation of monomers **1–4** with a number of aromatic diamines in the presence of TPP and Py. The results presented herein also demonstrate clearly that the incorporation of the benzazole ring as a pendent group into the polymer backbone remarkably enhanced the solubility and thermal stability of the polymers. Thus, they are considered to be new and promising processable high-temperature polymeric materials.

Figure 4 DSC curve of PEIA1b with a heating rate of 20°C/min in nitrogen.

References

1. Polyimides; Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds.; Chapman & Hall: New York, 1990; p 58.
2. Imai, Y. In Polyimides: Fundamentals and Applications; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; p 7.
3. Hergenrother, P. M.; Havens, S. J. Macromolecules 1994, 27, 4659.
4. Yan, J. L.; Wang, Z.; Gao, L. X.; Ding, M. X. Polymer 2005, 46, 7678.
5. Maya, E. M.; Lozano, A. E.; Campa, J. G.; Abajo, J. Macromol Rapid Commun 2004, 25, 592.
6. Imai, Y. In Polyimides: Fundamentals and Applications; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; p 49.
7. Teraza, C. A.; Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. J Polym Sci Part A: Polym Chem 2008, 46, 1510.
8. Li, W.; Li, S.; Zhang, Q.; Zhang, S. Macromolecules 2007, 40, 8205.
9. Bhuvana, S.; Sarojadevi, M. J Polym Res 2007, 14, 261.
10. Hamciuc, C.; Hamciuc, E.; Bruma, M. Polymer 2005, 46, 5851.
11. Huang, L. T.; Yen, H. J.; Chang, C. W.; Liou, G. S. J Polym Sci Part A: Polym Chem 2010, 48, 4747.
12. Wang, H. M.; Hsiao, S. H. Polym Chem 2010, 1, 1013.
13. Li, Z. X.; Fan, L.; Ge, Z. Y.; Wu, J. T.; Yang, S. Y. J Polym Sci Part A: Polym Chem 2003, 41, 1831.
14. Liaw, D. J.; Hsu, P. N.; Chen, W. H.; Liaw, B. Y. Macromol Chem Phys 2001, 202, 1483.
15. Behniafar, H.; Ghorbani, M. Polym Degrad Stab 2008, 93, 608.
16. Patil, P. S.; Pal, R. R.; Salunkhe, M. M.; Maldar, N. N.; Wadgaonkar, P. P. Eur Polym J 2007, 43, 5047.
17. Tsay, S. Y.; Tsai, M. F.; Chen, B. K. J Appl Polym Sci 2005, 95, 321.
18. Hu, Z.; Li, S.; Zhang, C. J Appl Polym Sci 2007, 106, 2494.
19. Lee, C.; Iyer, N. P.; Min, K.; Pak, H.; Han, H. J Polym Sci Part A: Polym Chem 2004, 42, 137.
20. Hsiao, S. H.; Yang, C. P.; Chen, C. W.; Liou, G. S. J Polym Res 2005, 12, 289.
21. Liou, G. S.; Chen, H. W.; Yen, H. J. Macromol Chem Phys 2006, 207, 1589.

22. Cheng, S. H.; Hsiao, S. H.; Su, T. H.; Liou, G. S. Polymer 2005, 46, 5939.

23. Liaw, D. J.; Chen, W. H. Polymer 2003, 44, 3865.

24. Shockravi, A.; Abouzari-Lotf, E.; Javadi, A.; Atabaki, F. Eur Polym J 2009, 45, 1599.

25. Toiserkani, H.; Saidi, K.; Sheibani, H. J Appl Polym Sci 2009, 114, 185.

26. Toiserkani, H.; Sheibani, H.; Saidi, K. Polym Adv Technol, 2011, 22, 1494.

27. Frazer, A. H. High Temperature Resistant Polymers; Interscience: New York, 1968.

28. Toiserkani, H. High Perform Polym 2011, DOI: 10.1177/0954008311421988.

29. Behniafar, H.; Akhlaghini, B.; Habibian, S. Eur Polym J 2005, 41, 1071.

30. Liaw, D. J.; Fan, C. L.; Lin, C. C.; Wang, K. L. J Appl Polym Sci 2004, 92, 2486.

31. Li, H.; Wang, D.; Fan, L.; Yang, S. Polym Int 2006, 55, 409.

32. Gaymans, R. J. In Synthetic Methods in Step-Growth Polymers; Rogers, M. E., Long, T. E., Eds.; Wiley-Interscience: Hoboken, NJ, 2003; p 135.