Novel Aromatic Polyamides Bearing Pendent Diphenylamino or Carbazolyl Groups

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ABSTRACT: Two new diamines, 2,4-diaminotriphenylamine (**3**) and *N*-(2,4-diaminophenyl)carbazole (**4**), were synthesized via the cesium fluoride-mediated aromatic substitution reactions of 1-fluoro-2,4-dinitrobenzene with diphenylamine and carbazole, followed by palladium-catalyzed hydrazine reduction. Amorphous and soluble aramids having pendent diphenylamino and carbazolyl groups were prepared by the phosphorylation polycondensation of aromatic dicarboxylic acids with diamines **3** and **4**, respectively. The aramids derived from diamine **3** had sufficiently high molecular weights to permit the casting of flexible and tough films. They exhibited excellent mechanical properties and moderately high softening temperatures in the 221–298 °C range. However, the reactions of diamine **4** with aromatic diacids gave relatively lower molecular weights products that could not afford flexible films. For a comparative purpose, the parent aramids derived from *m*-phenylenediamine and aromatic diacids were also prepared and characterized. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 3302–3313, 2004
Keywords: aromatic polyamides; aramids; triphenylamine; carbazole; 2,4-diaminotriphenylamine; *N*-(2,4-diaminophenyl)carbazole

INTRODUCTION

Wholly aromatic polyamides (aramids) have been well known for their high thermal stability, good chemical resistance, and excellent mechanical properties.[1–5] They are also known as difficult fabricable materials because of their high softening temperatures (T_s) and insoluble nature in most organic solvents. Because these problems restrict the further applications of the aramids, considerable efforts have been made to improve their properties by structural modification.[6–9] One of the common approaches to increasing solubility and lowering T_s is the attachment of bulky lateral groups along the polymer main chain. For example, soluble polyterephthalamides and polyisophthalamides with pendent phenoxy, phenylthio, and naphthoxy groups have been reported.[10–12]

Recently, we have reported the synthesis of soluble aromatic polyamides bearing triphenylamine units in the main chain based on 1,4-bis[*N*-(4-aminophenyl)-*N*-phenyl]phenylenediamine[13] and 1,4-bis[*N*-(4-carboxyphenyl)-*N*-phenyl]phenylenediamine,[14] respectively. Because of the incorporation of bulky, three-dimensional triphenylamine unit along the polymer backbone, all the polyamides were amorphous, had good solubility in many aprotic solvents, and exhibited excellent thin-film–forming capability. In a continuation of these

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studies, this work deals with the synthesis of two new diamines, 2,4-diaminotriphenylamine (**3**) and *N*-(2,4-diaminophenyl)carbazole (**4**), and their use in the preparation of modified aramids having bulky pendent diphenylamino or carbazolyl groups. The introduction of these bulky pendent groups would interrupt the chain–chain hydrogen bonding of the aramids and reduce chain packing efficiency and crystallinity. This should enhance solubility while maintaining high glass-transition temperatures (T_g) or T_s through decreased segmental mobility resulting from steric hindrance. In addition, the prepared triphenylamine- and carbazole-containing polyamides may find applications in organic electroluminescent elements because triphenylamine and carbazole derivatives and polymers are reputed to be hole-transporting layer materials.[15–20]

EXPERIMENTAL

Materials

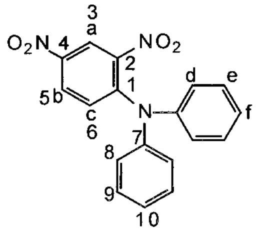
Diphenylamine (Acros), 1-fluoro-2,4-dinitrobenzene (Acros), carbazole (Acros), cesium fluoride (CsF; Acros), palladium on charcoal (Pd/C; Fluka), triphenyl phosphite (TPP; Acros), and hydrazine monohydrate (Acros) were used without further purification. Pyridine (Py; Wako) and *N*-methyl-2-pyrrolidone (NMP; Fluka) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. *m*-Phenylenediamine (TCI) was vacuum-distilled before use. The commercially available aromatic dicarboxylic acids such as terephthalic acid (**5a**; Wako), 4,4′-biphenyldicarboxylic acid (**5b**; TCI), 2,6-naphthalenedicarboxylic acid (**5c**; TCI), and 4,4′-dicarboxydiphenyl ether (**5d**; TCI) were used as received.

Monomer Synthesis

2,4-Dinitrotriphenylamine (1)

In a 250 mL round-bottom flask equipped with a stirring bar, a mixture of 30.4 g (0.18 mol) of diphenylamine, 33.5 g (0.18 mol) of 1-fluoro-2,4-dinitrobenzene, and 30 g of cesium fluoride (CsF) in 120 mL of dimethyl sulfoxide (DMSO) was heated at 120 °C for about 10 h. After cooling, the mixture was poured into 500 mL of ethanol, and the precipitate was collected by filtration and washed thoroughly with methanol and water. The crude product was recrystallized from ethanol to afford 45 g (yield 75 %) of pure dinitro compound **1** as orange crystals; mp = 182–183 °C (by DSC, 2 °C/min).

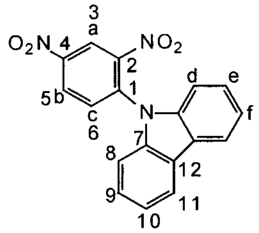
IR (KBr): 1535, 1338 cm^{-1} (—NO_2). ANAL. Calcd for $C_{18}H_{13}N_3O_4$ (335.32): C, 64.47 %; H, 3.91 %; N, 12.53 %. Found: C, 64.19 %; H, 3.80 %; N, 12.49 %. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.61 (d, J = 2.72 Hz, H_a), 8.19 (dd, J = 9.28, 2.72 Hz, H_b), 7.32 (t, J = 9.48 Hz, H_e), 7.25 (d, J = 9.28 Hz, H_c), 7.19 (t, J = 7.48 Hz, H_f), 7.06 (d, J = 7.44 Hz, H_d). ^{13}C NMR (DMSO-d_6, δ, ppm): 146.2 (C^1), 145.4 (C^7), 141.7 (C^4), 140.6 (C^2), 129.9 (C^9), 127.6 (C^3), 126.6 (C^5), 126.1 (C^{10}), 124.7 (C^8), 122.9 (C^6).



N-(2,4-Dinitrophenyl)carbazole (2)

According to the same procedure as described above, compound **2** was synthesized from the condensation of carbazole and 1-fluoro-2,4-dinitrobenzene with a 85 % yield and mp of 188–189 °C (by DSC, 2 °C/min).

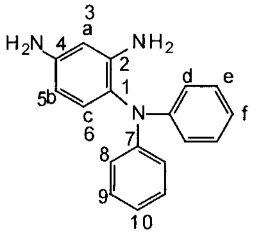
IR (KBr): 1541, 1340 cm^{-1} (—NO_2). ANAL. Calcd for $C_{18}H_{11}N_3O_4$ (333.30): C, 64.87 %; H, 3.53 %; N, 12.61 %. Found: C, 65.02 %; H, 3.22 %; N, 12.53 %. ^{1}H NMR (DMSO-d_6,δ, ppm): 9.01 (d, J = 2.60 Hz, H_a), 8.71 (dd, J = 8.75, 2.55 Hz, H_b), 8.12 (d, J = 7.70 Hz, H_g), 8.04 (d, J = 8.75 Hz, H_c), 7.41 (t, J = 7.30 Hz, H_e), 7.34 (t, J = 7.45 Hz, H_f), 7.16 (d, J = 8.15 Hz, H_d). ^{13}C NMR (DMSO-d_6, δ, ppm): 146.1 (C^4), 145.9 (C^2), 139.5 (C^7) 136.4 (C^6), 132.1 (C^9), 128.9 (C^1), 126.7 (C^{11}), 124.1 (C^{10}), 122.0 (C^{12}), 121.7 (C^8), 120.7 (C^5), 108.9 (C^3).



2,4-Diaminotriphenylamine (3)

In a 250 mL round-bottom flask equipped with a stirring bar, a mixture of 13.9 g (0.04 mol) of dinitro compound **1**, 0.2 g of 10% Pd/C, 15 mL of hydrazine monohydrate, and 150 mL of ethanol was heated at a reflux temperature for 8 h. The solution was filtered hot to remove Pd/C. On cooling, the product started to crystallize, and the next day the product was collected by filtration, and then dried in vacuum to afford 7.6 g (70 % yield) of pure diamine **3** as pale gray fine needles; mp = 155–156 °C (by DSC, 2 °C/min).

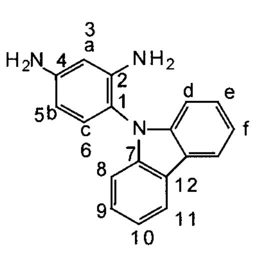
IR (KBr): 3475, 3378 cm^{-1} (—NH$_2$). ANAL. Calcd for $C_{18}H_{17}N_3$ (275.35): C, 78.52%; H, 6.22 %; N, 15.26 %. Found: C, 77.18 %; H, 6.25 %; N, 15.03 %. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.18 (t, J = 8.36 Hz, H$_e$), 7.05 (d, J = 7.72 Hz, H$_d$), 6.88 (t, J = 7.28 Hz, H$_f$), 6.82 (d, J = 8.04 Hz, Hc), 6.09 (dd, J = 8.04, 2.52 Hz, H$_b$), 6.07 (s, H$_a$). ^{13}C NMR (DMSO-d_6, δ, ppm): 147.1 (C^7), 146 (C^4), 144.7 (C^2), 131.3 (C^6), 129.1 (C^9), 123.8 (C^1), 121.2 (C^{10}), 120.6 (C^8), 106.8 (C^5), 102.5 (C^3).



N-(2,4-Diaminophenyl)carbazole (4)

Diamine **4** was synthesized from the reduction of dinitro compound **2** by a similar procedure as that described above. The diamine was obtained as off-white, fine needles in a 76 % yield; mp = 130–131 °C (by DSC, 2 °C/min).

IR (KBr): 3384, 3303 cm^{-1} (—NH$_2$). ANAL. Calcd for $C_{18}H_{15}N_3$ (273.34): C, 79.10 %; H, 5.53 %; N, 15.37 %. Found: C, 78.67 %; H, 5.45 %; N, 15.35 %. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.12 (d, J = 7.75 Hz, H$_g$), 7.37 (t, J = 7.25 Hz, H$_e$), 7.25 (t, J = 7.20 Hz, H$_f$), 7.21 (d, J = 8.10 Hz, H$_d$), 6.97 (d, J = 8.25 Hz, H$_c$), 6.18 (dd, J = 8.25, 2.50 Hz, H$_b$), 6.13 (d, J = 2.40 Hz, H$_a$). ^{13}C NMR (DMSO-d_6, δ, ppm): 147.7 (C^4), 144.9 (C^2), 141.2 (C^7), 130.5 (C^6), 125.9 (C^{11}), 123.1 (C^{12}), 120.2 (C^9), 119.6 (C^{10}), 113.6 (C^1), 110.1 (C^8), 106.2 (C^5), 101.9 (C^3).



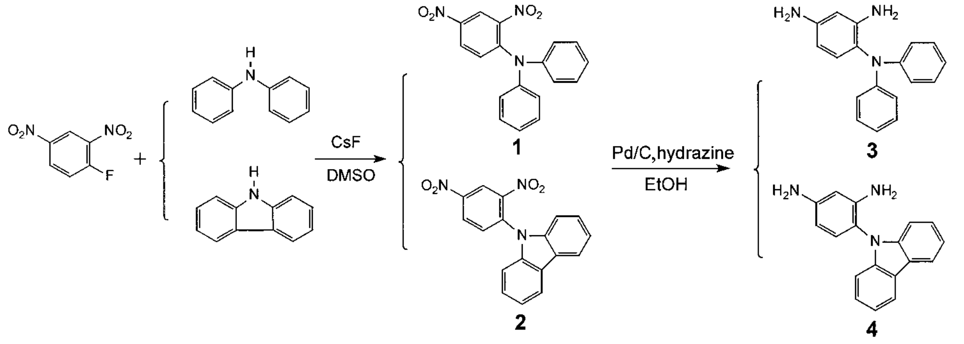
Polymer Synthesis

The synthesis of polyamide **7a** is used as an example to illustrate the general synthetic route used to produce the polyamides. A 50 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.413 g (1.50 mmol) of diamine **3**, 0.249 g (1.50 mmol) of terephthalic acid (**5a**), 1.2 mL of TPP, 2 mL of NMP, 0.5 mL of pyridine, and 0.2 g of calcium chloride ($CaCl_2$). The reaction mixture was heated with stirring at 120 °C for 3 h. The resultant solution was poured slowly into 300 mL of methanol. The precipitate was washed thoroughly with methanol and hot water and then collected by filtration. The inherent viscosity of the polymer **7a** was 0.46 dL/g, measured at a concentration of 0.5 g/dL in DMAc containing 5 wt% LiCl at 30 °C.

IR (film): 3300 (N—H stretch), 1668 (C═O stretch), 1525 (N—H bending), 1419 (amide C—N stretch), 1271 cm^{-1} (NAr$_3$ C—N stretch). ^{1}H NMR (DMSO-d_6, δ, ppm): 10.53, 10.44, 9.20, 9.10 (amide protons), 6.97–9.21 (m, aromatic protons). ^{13}C NMR (DMSO-d_6, δ, ppm): 165.11, 164.93, 164.64, 164.48 (amide carbons), 121.91–146.61 (m, aromatic carbons).

Measurements

Elemental analyses were run in a Heraeus Vario-III analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Jeol EX-400 spectrometer using DMSO-d_6 as the solvent and tetramethylsilane as internal reference. Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. Weight-average molecular weights and number-average molecular weights were obtained via size exclusion chromatography (SEC) on the basis of polystyrene calibration using a Water 2410 apparatus and tetrahydrofuran (THF) as the eluent. The inherent viscosities were determined at a concentration of 0.5 g/dL in DMAc containing 5 wt% LiCl using a Cannon-Fenske viscometer at 30 °C. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris 1 DSC differential scanning calorimeter in flowing nitrogen (20 cm^3/min) at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a scan rate of 10 °C/min with a penetration probe of 1.0 mm diameter under an applied constant load of 10 mN. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were car-



Scheme 1

ried out on 3–5 mg samples heated in flowing nitrogen or air (30 cm^3/min) at heating rate of 20 °C/min. Measurements were performed with film specimens of about 0.1 mm in thickness. An Instron universal tester model 4400R with a load cell 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm width, 6 cm length, and about 0.1 mm thickness), and an average of at least three replicas was used. Wide-

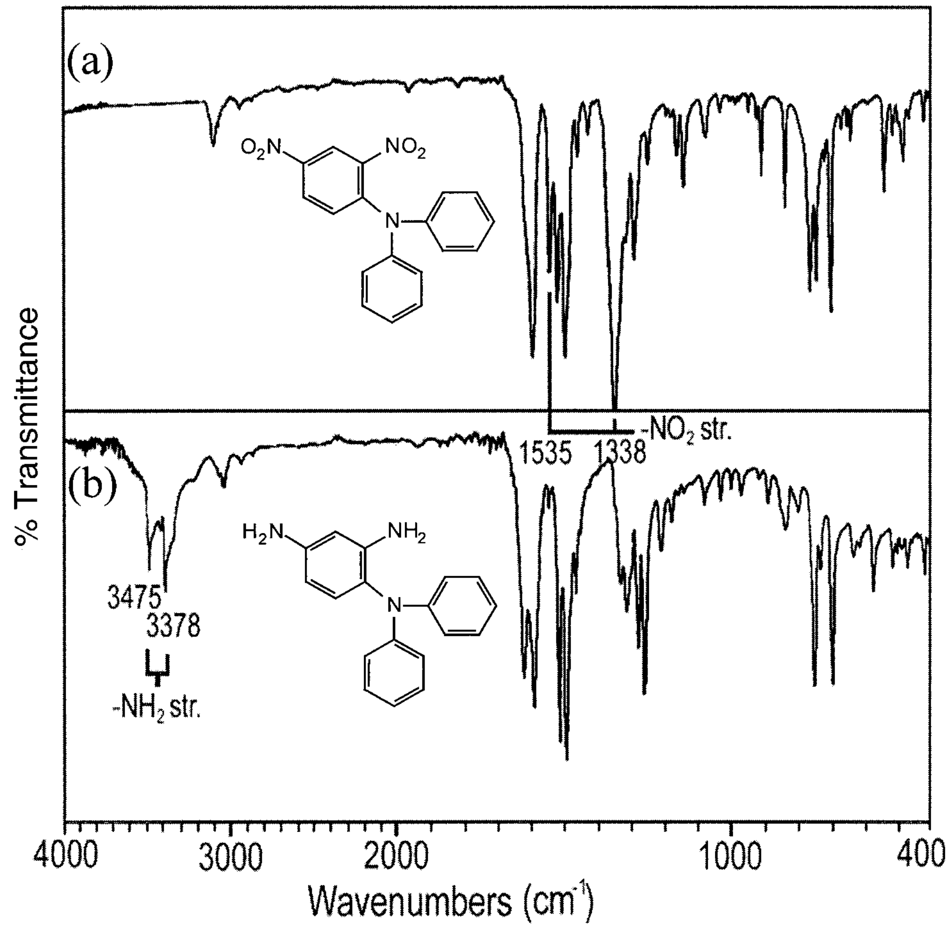


Figure 1. IR spectra of (a) dinitro compound **1** and (b) diamine **3**.

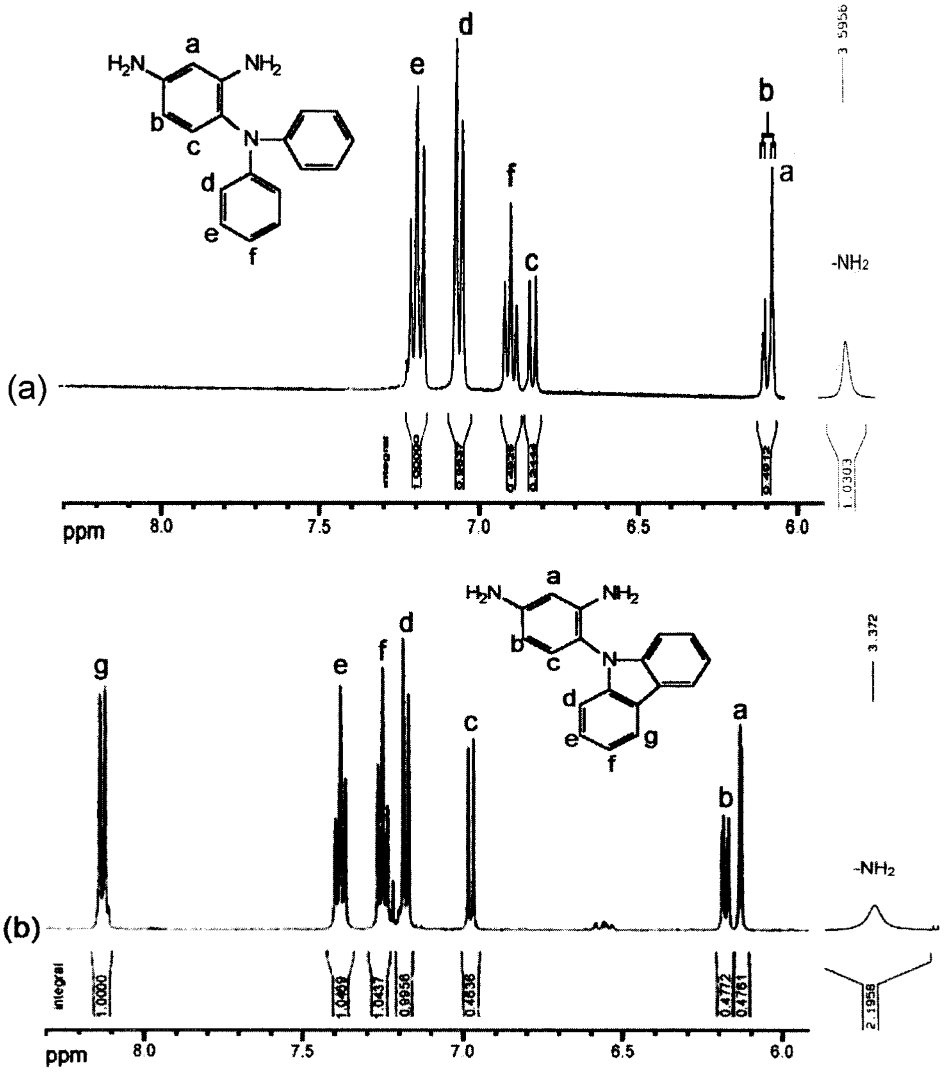


Figure 2. ^{1}H NMR spectra of (a) diamine **3** and (b) diamine **4** in $CDCl_3$.

angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer with a graphite monochromator, using nickel-filtered Cu Kα radiation (λ = 1.5418 Å, operating at 40 kV and 20 mA). The scanning rate was 3 °/min over a 2θ range of 5–45°.

RESULTS AND DISCUSSION

Monomer Synthesis

Two aromatic diamines having bulky pendent groups, 2,4-diaminotriphenylamine (**3**) and *N*-(2,4-diaminophenyl)carbazole (**4**), were prepared by the synthetic route outlined in Scheme 1. The first step involved a nucleophilic aromatic fluoro-displacement of 1-fluoro-2,4-dinitrobenzene with diphenylamine and carbazole, respectively, in the presence of cesium fluoride in DMSO. The CsF-assisted aromatic nucleophilic substitution reaction has been demonstrated as an efficient method in the synthesis of functional compounds[21–24] and aromatic polyethers and polysulfides.[25,26] Diamines **3** and **4** were readily obtained in high yields by the Pd/C-catalyzed reduction of the intermediate dinitro compounds **1** and **2** with hydrazine monohydrate in refluxing ethanol.

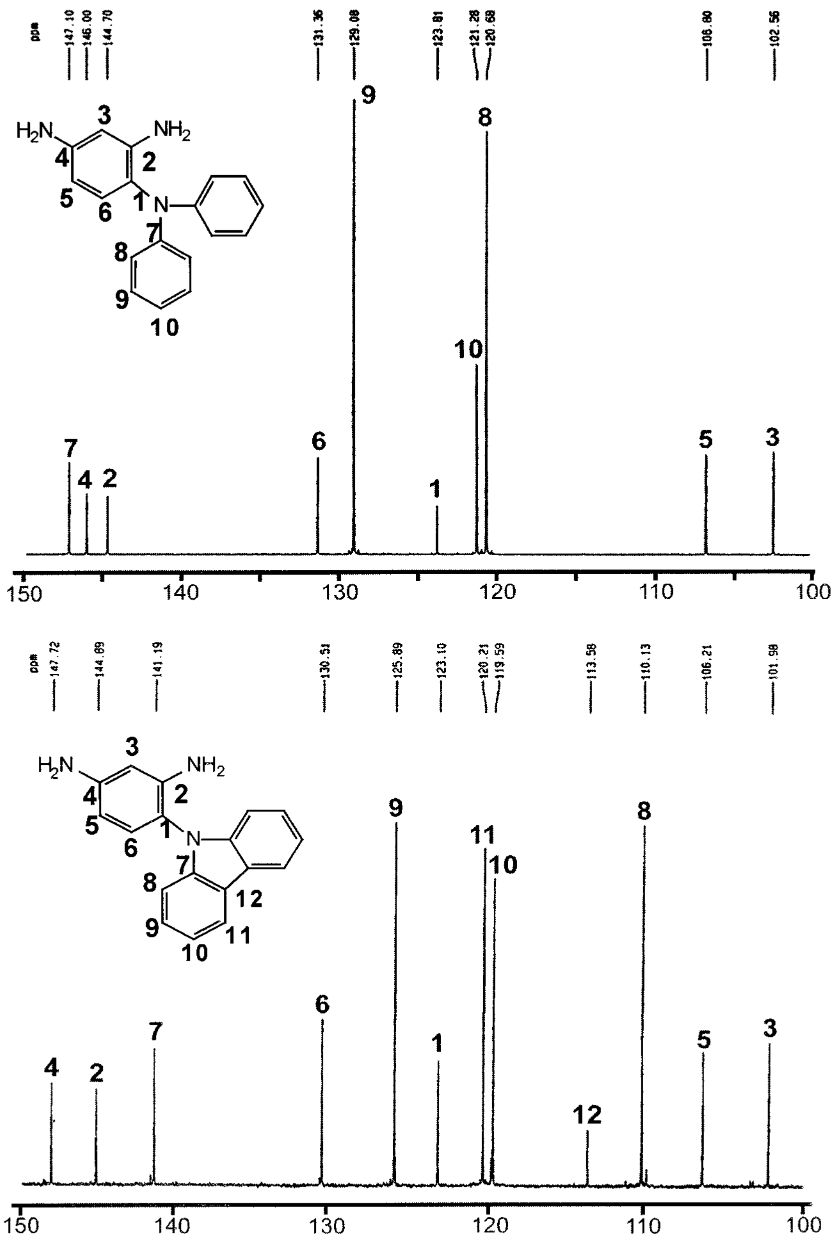
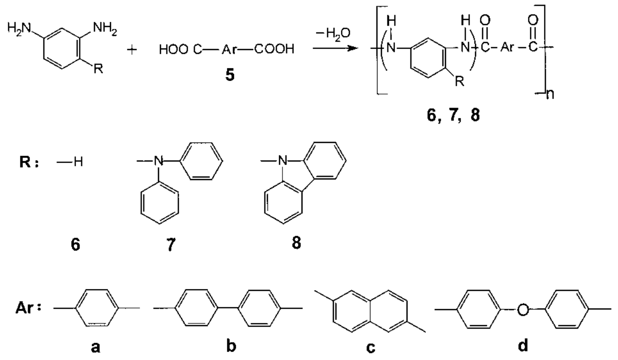


Figure 3. ^{13}C NMR spectra of (a) diamine **3** and (b) diamine **4** in $CDCl_3$.

Characterization by IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and elemental analysis indicated high purity with the data consistent with the expected molecular structures. The IR spectra of dinitro compound **1** and diamine **3** are illustrated in Figure 1. The nitro group of **1** gave two characteristic bands at 1535 and 1338 cm^{-1}, which disappeared after reduction. Diamine **3** showed a typical —NH_2 stretching absorption pair at 3475 and 3378 cm^{-1}. The ^1H NMR and ^{13}C NMR spectra of diamines **3** and **4** are shown in Figure 2 and Figure 3, respectively. The assign-



Scheme 2

Table 1. Inherent Viscosity, Molecular Weights, Film Quality, and Solubility Behavior of Polyamides

Polymer Code	η_{inh}[a] (dL/g)	M_n[b]	M_w[b]	M_w/M_n	Film Quality	Solubility in Various Solvents[c]					
						NMP	DMAc	DMSO	DMF	*m*-Cresol	THF
6a	0.76				Brittle	−	−	−	−	−	−
6b	0.66				Brittle	−	−	−	−	−	−
6c	0.60				Brittle	−	−	−	−	−	−
6d	1.52				Flexible	+	+	+	+	+h	−
7a	0.50	10400	16300	1.57	Flexible	+	+	+	+	+	+
7b	0.45	8900	14300	1.60	Flexible	+	+	+	+	+	+
7c	0.46	9200	17900	1.95	Flexible	+	+	+	+	+	+
7d	0.54	11500	23000	2.00	Flexible	+	+	+	+	+	+
8a	0.30	5300	8300	1.57	Brittle	+	+	+	+	+	+
8b	0.27	4600	6700	1.46	Brittle	+	+	+	+	+	+
8c	0.28	4900	7200	1.47	Brittle	+	+	+	+	+	+
8d	0.38	7500	11900	1.59	Brittle	+	+	+	+	+	+

[a] Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt% LiCl at 30 °C.

[b] Relative to polystyrene standard, using THF as the eluent.

[c] Qualitative solubility was tested with 10 mg sample in 1 mL solvent.

+, soluble at room temperature; +h, soluble on heating; −, insoluble even on heating; NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

ments of each carbon and proton are also given in the figures, and these spectra agree well with the proposed structures. It is worth mentioning that the hydrogens Hd-g of diamine **4** have larger chemical shifts than the corresponding ones (Hd-f) of diamine **3** due to the larger anisotropic field that is generated by the carbazole conjugated system.

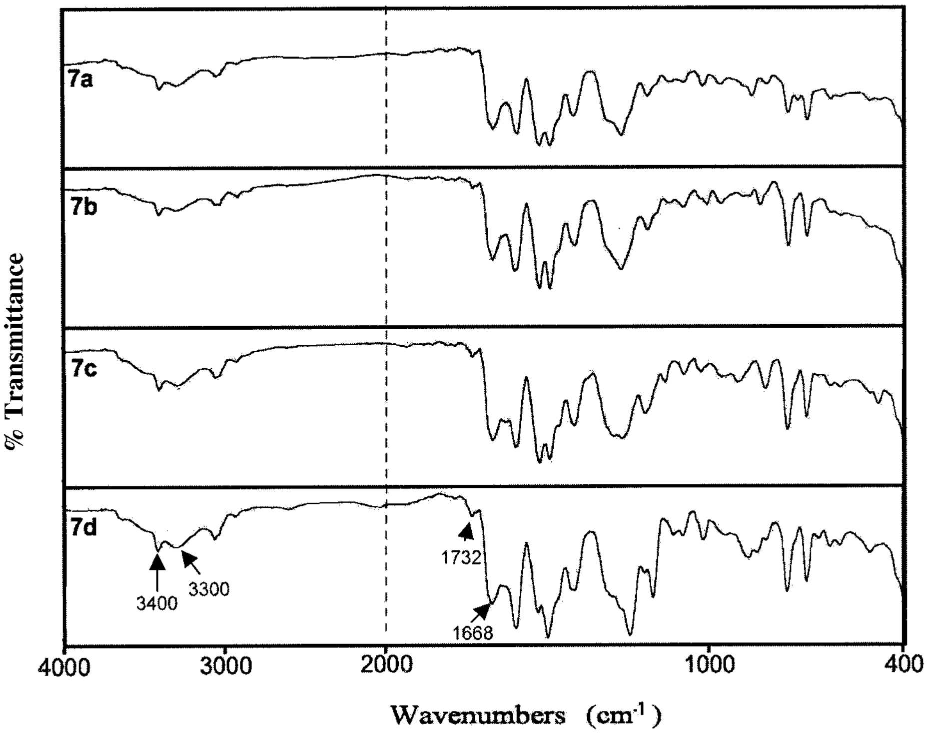


Figure 4. Thin film FTIR spectra of polyamides **7a–d**.

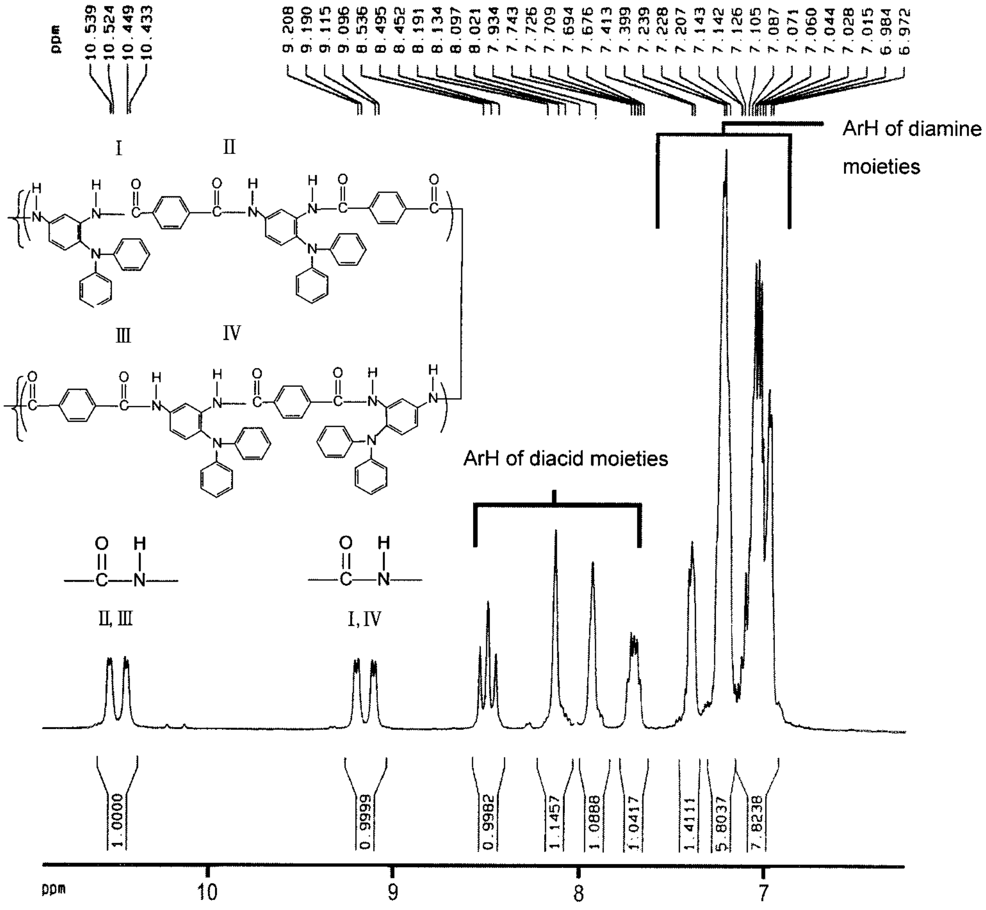


Figure 5. The ^{1}H NMR spectrum of polyamide **7a** in DMSO-d_6.

Polymer Synthesis

A new class of aramids bearing pendent diphenylamino or carbazolyl groups, **7a–d** and **8a–d**, were prepared from the direct polycondensation of diamines **3** and **4**, respectively, with aromatic dicarboxylic acids **5a–d** by means of TPP and pyridine.[27] The corresponding parent aramids (**6a–d**) were also synthesized to compare their physical and mechanical properties with those of the aramids with the pendent groups. The structures and codes of all aramids can be seen from Scheme 2. The parentheses in the formulas of these polymers indicate that the asymmetric moieties of diamines **3** and **4** may appear in the polymer chain as shown or in the reverse orientation. For the **7** and **8** series, all polycondensations proceeded readily in homogeneous and transparent solutions, and the aramids were isolated as fibers or powders in quantitative yields. Inherent viscosities for **7a–d** ranged from 0.46 to 0.54 dL/g, which correspond to an estimated number-average molecular weight (M_n) of 8900–10400 g/mol and weight-average molecular weight (M_w) of 14300–23000 on the basis of SEC results (Table 1). The molecular weights of the **7** series aramids were sufficiently high for the casting of flexible and creasable films. However, aramids **8a–d** were produced with comparatively lower inherent viscosities (0.27–0.38 dL/g) and molecular weights (M_n = 4600–7500 and M_w = 6700–11900), and all of them could not afford free-standing films. One may think the formation of low-molecular-weight polymers is possibly attributed to the use of impure diamine monomer. We exclude the possibility of doubt bcause the diamine **4** was pure white with a sharp melting temperature range of 130–131 °C. We propose, therefore, that the low molecular weight might be a result of the steric hindrance caused by the bulky carbazolyl group *ortho* to one of the amino groups in diamine **4**. The diphenylamino group in diamine **3** has a higher conformational flexibility

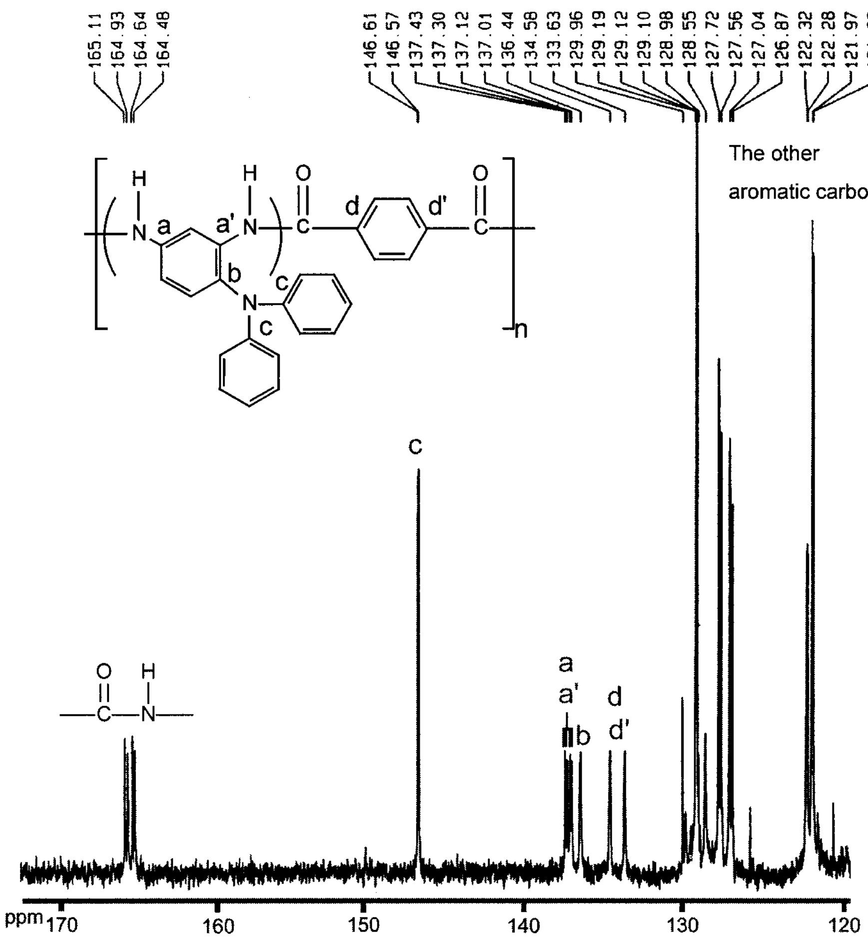


Figure 6. The ^{13}C NMR spectrum of polyamide **7a** in DMSO-d_6.

than the carbazolyl group in diamine **4**; therefore, diamine **3** is more reactive than diamine **4**. During the synthesis of the unmodified aramids **6a–c**, an early precipitation occurred due to the insolubility. The insoluble nature of these aramids could be attributable to the their high crys-

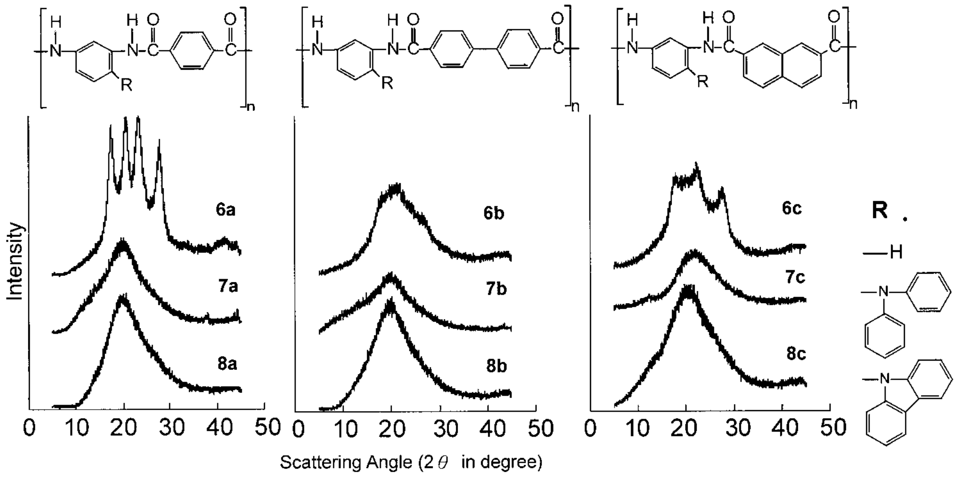


Figure 7. WAXD patterns of the polyamides.

tallinity, as shown by X-ray diffractometry. The cast films of aramids **6a–c** were highly brittle. Soluble aramid **6d** was obtained with a high inherent viscosity up to 1.52 dL/g and could be cast into flexible and tough film because of its more flexible backbone.

Structural features of these polyamides were verified by FTIR spectra based on characteristic absorption bands observed around 3300 (N—H stretching), 1670 (C═O stretching), 1525 (N—H bending), and 1270 cm^{-1} (C—N stretching). Figure 4 illustrates the FTIR spectra of the **7** series polyamides. Additional features of these spectra worth mentioning are the medium spike and weak shoulder peaks appearing around 3420 and 1730 cm^{-1}, respectively. It is well known that, in general, NH and carbonyl absorptions arising from non–H-bonded amide groups appear at higher frequencies than those arising from the associated state.[28] Therefore, the observed spike and shoulder peaks may correspond to a significant fraction of nonassociated amide groups present in these polyamides. This implies that the bulky group *ortho* to the amide group may sterically hinder the formation of intermolecular hydrogen bonding. Solution ^{1}H and ^{13}C NMR spectra in DMSO-d_6 confirmed the chemical structures of the prepared aramids with amide proton chemical shifts observed in the region of 9–11 ppm and the amide carbonyl peaks at around 165 ppm. Example spectra are shown in Figures 5 and 6. In the ^{1}H NMR spectrum of aramid **7a**, peaks in the regions of 9.0–9.2 and 10.4–10.5 ppm correspond to the amide protons of the two possible segments shown in Figure 5. Aramid **7a** also showed four amide carbonyl peaks in its ^{13}C NMR spectrum because of the nonsymmetric nature of the diamine component. The near equal intensity of amide proton and carbonyl resonances suggests a statistical random distribution of the asymmetric diamine moieties in the polymer chain.

Table 2. Thin Film Tensile Properties of Polyamides

Polymer Code	Strength to Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
6d	98	11	2.1
7a	85	7	1.9
7b	98	9	2.1
7c	101	9	2.1
7d	102	9	2.3

Films were cast by evaporation of polymer solutions in DMAc. The cast films were dried under vacuum at 150 °C for 6 h prior to the tensile test.

Table 3. Thermal Properties of Polyamides

Polymer Code	T_g[a] (°C)	T_s[b] (°C)	T_d[c] (°C) In N_2	T_d[c] (°C) In Air	Char Yield[d] (wt %)
6a	—	—	524	481	65
6b	—	—	531	516	69
6c	—	—	538	514	68
6d	232	218	510	500	68
7a	—	281	500	470	70
7b	—	298	512	491	77
7c	—	288	494	492	77
7d	224	221	484	478	62
8a	—	—	462	499	74
8b	—	—	535	514	69
8c	—	—	487	518	78
8d	211	208	491	511	71

[a] The samples were heated from 30 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 30 °C at −100 °C/min in nitrogen. The midpoint temperature of baseline shift on the subsequent DSC trace (from 30 to 400 °C at 20 °C/min) was defined as T_g.

[b] Softening temperature taken as the onset temperature of the probe displacement on the TMA trace. The samples were heated at 250 °C for 30 min prior to the TMA test.

[c] Decomposition temperature at which a 10 wt % loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 30 cm^3/min.

[d] Residual weight percent at 800 °C in nitrogen.

Properties of Polymers

The solubility properties of all aramids are also reported in Table 1. All the pendent group-containing aramids **7a–d** and **8a–d** were readily soluble in all the organic solvents tested. However, all the parent aramids except **6d** were insoluble in these solvents. The insolubility associated with aramids **6a–c** could be attributed to their semicrystalline nature, as shown by the WAXD patterns displayed in Figure 7. Apparently, the bulky diphenylamino and carbazolyl groups interfere with the efficient chain packing and decrease the chain–chain interactions, resulting in a decreasing crystallinity and an enhanced solubility.

As mentioned earlier, polyamides **6d** and **7a–d** could be solution-cast into smooth, flexible, and tough films. These films were subjected to tensile testing, and the tensile properties are presented in Table 2. The tensile strengths, elongations to break, and initial moduli of these films were in

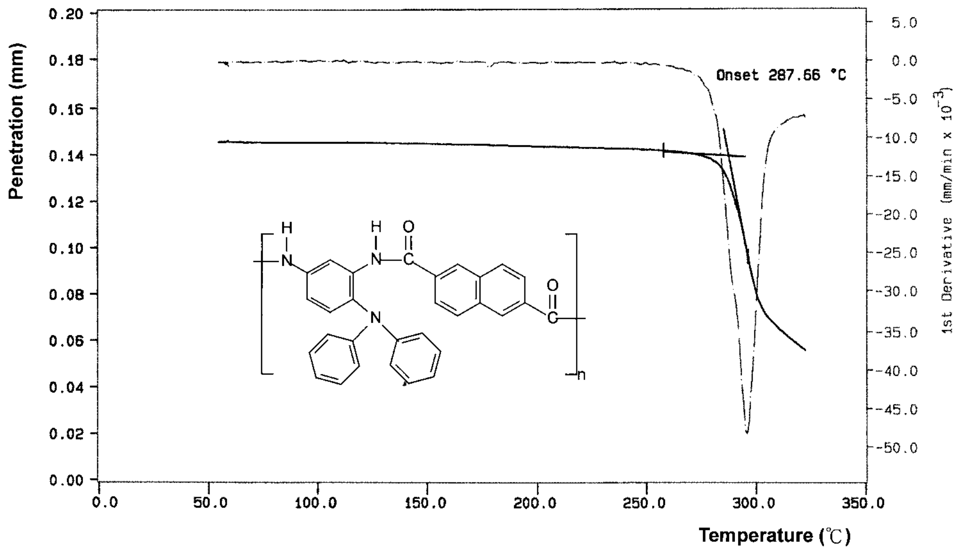


Figure 8. TMA curve of polyamide **7c** with a heating rate of 10 °C/min.

the range of 85–102 MPa, 7–11 %, and 1.9–2.3 GPa, respectively, indicative of strong and tough polymeric materials.

TGA, TMA, and DSC were employed to evaluate the thermal properties of all polyamides. The thermal behavior data are summarized in Table 3. DSC was used to determine the thermal transitions of all the polyamides. However, except for the polyamides derived from the flexible diacid **5d**, all polyamides did not show discernible glass transitions on the DSC traces, probably due to the rigid nature of their backbones. The softening temperatures (T_s) of some polymer film samples have also been measured by TMA. The T_s value was read from the onset temperature of probe displacement by TMA. Figure 8 illustrates a typical TMA curve of polyamide **7c**. The T_s values of the **7** series polyamides were between 221 and 298 °C. TGA revealed that all polymers exhibited reasonable thermal stability. The 10 % weight loss temperatures (T_d) of the polymers were in the range of 470–518 °C in nitrogen and 462–538 °C in air. The amount of carbonized residue (char yield) at 800 °C in nitrogen for all polyamides were in the range of 62–78 wt%. The high char yields of these polyamides can be ascribed to their high aromatic content.

CONCLUSIONS

New aromatic polyamides with diphenylamino and carbazolyl pendent groups were synthesized from the polycondensation reactions of two new diamines with various aromatic dicarboxylic acids. These polyamides showed an enhanced solubility and decreased crystallinity but slightly lower thermal stability than the corresponding counterparts without the pendent groups. The polymers derived from *N*-(2,4-diaminophenyl)carbazole exhibited relatively lower molecular weights and could not afford useful films. However, the polymers based on 2,4-diaminotriphenylamine had sufficiently high molecular weights for the casting of strong and tough films. These films displayed softening temperatures in the range 221–298 °C and a reasonable thermal stability.

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