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Synthesis and Characterization of Novel Carbazole-Containing Soluble Polyimides

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ABSTRACT: Three new carbazole-based diamines, 3,6-diaminocarbazole (**2**), 3,6-diamino-*N*-phenylcarbazole (**4**) and *N*-(4′-aminophenyl)-3-aminocarbazole (**7**), were prepared from carbazole or *N*-phenylcarbazole. Homopolyimides and copolyimides derived from these three diamines as well as 4,4′-diamineodiphenyl ether (DDE), with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) in 1-methyl-2-pyrrolidinone (NMP) via a two-step condensation reaction, were obtained. These polyimides, especially those derived from monomers **4** and **7**, were readily soluble in many organic polar solvents. They had weight-average molecular weights ranging from 1.5×10^4 to 5.9×10^4. DSC analyses indicated that (co)polyimides derived from diamine **4** had glass transition temperatures and others derived from diamines **2** and **7** did not show any glass transition prior to thermal decomposition in air.

Introduction

Aromatic polyimides exhibit excellent thermal, mechanical and electrical properties and have been used in electronic, coating, and other industries.[1] They can be synthesized from the conventional polycondensation of A−A and B−B monomers, namely, an aromatic dianhydride and an aromatic diamine. Many rodlike polyimides, however, are insoluble in common organic solvents due to their rigid backbones, thus limiting their applications. To overcome such a difficulty, polymer structure modification becomes necessary. There are a few ways to modify polymer structures, such as introduction of pendent groups (aromatic or alkyl groups) onto the polymer chains[2−6] and incorporation of noncoplanar structural units in the main chains.[9] To achieve such a goal, of course, it is necessary to design and synthesize new monomers, either diamine or dianhydride or both, which can fulfill this requirement. Much effort has been achieved in designing and synthesizing new dianhydrides[10,11] and/or diamines,[12−16] thus, producing a great variety of soluble and processable polyimides for various purposes.

Carbazole is a compound which has been the subject of many studies, due to its photoconductive properties and its ability to form charge-transfer complexes, due to its inherent electrodonating nature arising from the nitrogen atom through the conjugated aromatic rings.[17] Carbazole and its many derivatives can be functionalized[18] and thus have been covalently incorporated into polymeric systems, both in main-chain[19−23] as building blocks and in side-chains as pendent groups.[24−27] It is quite likely that carbazole-containing polymers will possess electro- and photochemical properties as well as high thermal stability due to the carbazole conjugated system. It is thus worthy exploring the feasibility of difunctionalizing the carbazole compounds, introducing them into high-performance polyimides system.

We report here the synthesis of three new carbazole-based diamines, their polycondensations with a dianhydride, and the characterization of the resulting (co)polyimides.

Experimental Section

Materials. Carbazole, *N*-phenylcarbazole, copper(II) nitrate hemipentahydrate ($Cu(NO_3)_2 \cdot 2.5H_2O$), 1-iodo-4-nitrobenzene, anhydrous tin(II) chloride ($SnCl_2$), acetic acid, and acetic anhydride were purchased from Aldrich Chemical Co. and used as received. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) (99%, Aldrich Chemical Co.) was recrystallized from acetic anhydride and dried at 100 °C under high vacuum for 48 h. 4,4′-Diamineodiphenyl ether (DDE) was recrystallized from methanol and dried at 100 °C under high vacuum overnight. 1-Methyl-2-pyrrolidinone (NMP) was vacuum-distilled off from calcium hydride.

Measurements. NMR spectra were recorded on a Bruker AC−F200 spectrometer or on a Bruker AM-400 spectrometer in $CDCl_3$, acetone-d_6 or DMSO-d_6. UV−vis spectra were recorded on a Hewlett-Packard UV−vis spectrophotometer in THF at room temperature. Gel permeation chromatography (GPC) analysis was performed on a Waters Associates model 400 liquid chromatograph equipped with a UV (254 nm) detector using THF as an eluent at a rate of 1.0 mL/min and polystyrene as standards. Thermal analysis was performed on a differential scanning calorimeter (DSC) with a Mettler TA3000 system equipped with a TC10A TA processor and a

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DSC30 head at a heating rate of 20 °C/min on the first heating and at 10 °C/min on the second heating after cooling in air. Mass spectra were obtained on a VG Quattro mass spectrometer. IR spectra (KBr, pellets) were recorded on a Bomem MB-120 FTIR spectrophotometer.

Monomer Synthesis. 3,6-Dinitrocarbazole (1). $Cu(NO_3)_2 \cdot 2.5H_2O$ (14 g, 60 mmol) was added into a mixture of acetic acid (25 mL) and acetic anhydride (50 mL) at room temperature. The mixture was stirred for 10 min, and to this solution was then added carbazole (8.35 g, 50 mmol) slowly in portions over 5 min. Heat was generated during the addition (temperature rised to around 100 °C), and an additional 25 mL of acetic acid was added. The mixture was stirred at this temperature for 15 min and then poured into distilled water (500 mL). The precipitate was collected by filtration, washed with water (300 mL × 3). The still wet product was then dissolved into a potassium alcoholic aqueous solution (KOH 50 g, water 500 mL, and ethanol 500 mL). The solution turned red. After being stirred for 30 min, the solution was filtrated and the filtrate was acidified with concentrated hydrochloric acid. The yellow precipitate was then collected by filtration, washed with water and dried at 100 °C under vacuum. The yield was 11.0 g (85%): mp 240 °C (DSC in air); IR (KBr) 3395, 3082, 1634, 1612, 1579, 1517, 1307, 1102, 752, 718 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 11.10 (s, br, 1H, NH), 9.34 (d, 2H, $J = 2.3$ Hz, carbazole 4 and 5), 8.40 (dd, 2H, $J = 2.3$ Hz, $J = 8.9$ Hz, carbazole 2 and 7), 7.78 (d, 2H, $J = 8.9$ Hz, carbazole 1 and 8); MS (EI, *m*/*e*, % relative intensity) 257 (M^+, 100).

3,6-Diaminocarbazole (2). The dinitro compound **1** (2.57 g, 10.0 mmol) and $SnCl_2$ (19.0 g, 100 mmol), along with acetic acid (60 mL) and concentrated hydrochloric acid (10 mL), were placed into a round-bottom flask. The mixture was refluxed under argon for 24 h. The resulting solution was poured into an aqueous sodium hydroxide solution (20%, 500 mL). The precipitate was collected by filtration, washed with water, and dried at 70 °C under vacuum overnight. The product was then extracted with THF. Removal of the solvent afforded the crude product. The product was purified by recrystallization from ethanol under argon to give shiny gray solid: 1.50 g (76%): mp 255 °C (dec, DSC in air); IR (KBr) 3388, 3286, 3188, 1632, 1577, 1503, 1331, 1222, 1168, 868, 807, 712 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 1H, NH), 7.06 (d, 4H, $H_{1,4,5,8}$), 6.66 (dd, 2H, $H_{2,7}$, $J = 2.0$ Hz, $J = 8.5$ Hz), 4.54 (s, br, 4H, $2NH_2$); UV−vis (THF, λ_{max}) 326, 380 nm; MS (EI, *m*/*e*, % relative intensity) 197 (M^+, 100).

Anal. Calcd for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.31. Found: C, 72.50; H, 5.53; N, 20.69. The discrepancies in the elemental analysis may be due to the relative instability of the diamine in the air. The sample was sent to outside elemental analysis in an ordinary package, not under inert atmosphere, and the analysis was performed after a few days. In contrast, spectral analysis and polymerization were performed immediately after synthesis.

3,6-Dinitro-*N*-phenylcarbazole (3). $Cu(NO_3)_2 \cdot 2.5H_2O$ (10 g, 43 mmol) was added to a mixture of acetic acid (15 mL) and acetic anhydride (25 mL) at room temperature. The mixture was stirred for 10 min, and to this solution was then added *N*-phenyl-carbazole (4.00 g, 16.4 mmol) in portions over 5 min. The reaction temperature was controlled at around 30 °C by using a water bath. The mixture was stirred at this temperature for 30 min and then poured into distilled water (200 mL). The precipitate was collected by filtration, washed with water (300 mL × 3) and air-dried. The product was recrystallized from 1,2-dichlorobenzene. The yield was 5.20 g (95%): mp 280 °C (DSC in air); IR (KBr) 1670, 1590, 1519, 1493, 1467, 1337, 1274, 1225, 1163, 1105, 832, 753, 694 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.13 (d, 2H, $J = 2.2$ Hz), 8.40 (dd, 2H, $J = 2.2$ Hz, $J = 9.0$ Hz), 7.5−7.7 (m, 5H), 7.40 (d, 2H, $J = 9.0$ Hz); MS (EI, *m*/*e*, % relative intensity) 333 (M^+, 100).

3,6-Diamino-*N*-phenylcarbazole (4). Compound **3** (4.00 g, 12.0 mmol) and $SnCl_2$ (25.00 g, 131.86 mmol), along with acetic acid (60 mL) and concentrated hydrochloric acid (10 mL), were placed into a round-bottom flask. The mixture was refluxed under argon for 24 h. The resulting clear solution was poured into an aqueous sodium hydroxide solution (20%, 500 mL). The precipitate was collected by filtration, washed with water, and dried at 70 °C under vacuum overnight. The product was then extracted with THF. After removal of the solvent, the product was further purified through a flash column eluted with acetone and then recrystallized from a mixture of ethanol and water (9:1, v/v) under argon to give light gray needlelike crystals: 2.50 g (76%); mp 157 °C (DSC in air); IR (KBr) 3229, 3212, 1658, 1590, 1500, 1448, 1363, 1212, 830, 750, 699 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.58 (t, 2H, $H_{3',5'}$, $J = 8.4$ Hz), 7.52 (d, 2H, $H_{2'6'}$, $J = 8.4$ Hz), 7.36 (dt, 1H, $H_{4'}$, $J = 1.2$ Hz, $J = 7.6$ Hz), 7.15 (d, 2H, $H_{4,5}$, $J = 2.0$ Hz), 7.11 (d, 2H, $H_{1,8}$, $J = 8.8$ Hz), 6.70 (dd, 2H, $H_{2,7}$, $J = 8.8$ Hz, $J = 2.0$ Hz), 4.76 (s, br, 4H, $2NH_2$); UV−vis (THF, λ_{max}) 322, 384 nm; MS (EI, *m*/*e*, % relative intensity) 273 (M^+, 100).

Anal. Calcd for $C_{18}H_{15}N_3$: C, 79.10; H, 5.53; N, 15.37. Found: C, 78.54; H, 5.50; N, 15.34.

***N*-(4′-Nitrophenyl)-carbazole (5).** Into a round-bottom flask were placed carbazole (1.67 g, 10.0 mmol), 1-iodo-4-nitrobenzene (2.02 g, 10.0 mmol), copper powder (1 g), powdered anhydrous potassium carbonate (1.4 g), and nitrobenzene (25 mL). The mixture was refluxed under argon for 24 h. The hot solution was then filtrated through a glass sinter filter, and the solvent was distilled off under reduced pressure. The product was purified through a flash column eluted with dichloromethane, and then recrystallized from ethyl acetate twice to afford a light-yellow crystalline product: 1.72 g (60%); mp 120−122 °C; IR (KBr) 1608, 1592, 1500, 1453, 1228, 852, 751, 726, 694 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.47 (d, 2H, $J = 9.0$ Hz), 8.13 (d, 2H, $J = 7.9$ Hz), 7.78 (d, 2H, $J = 9.0$), 7.3−7.5 (m, 6H); MS (EI, *m*/*e*, % relative intensity) 288 (M^+, 100).

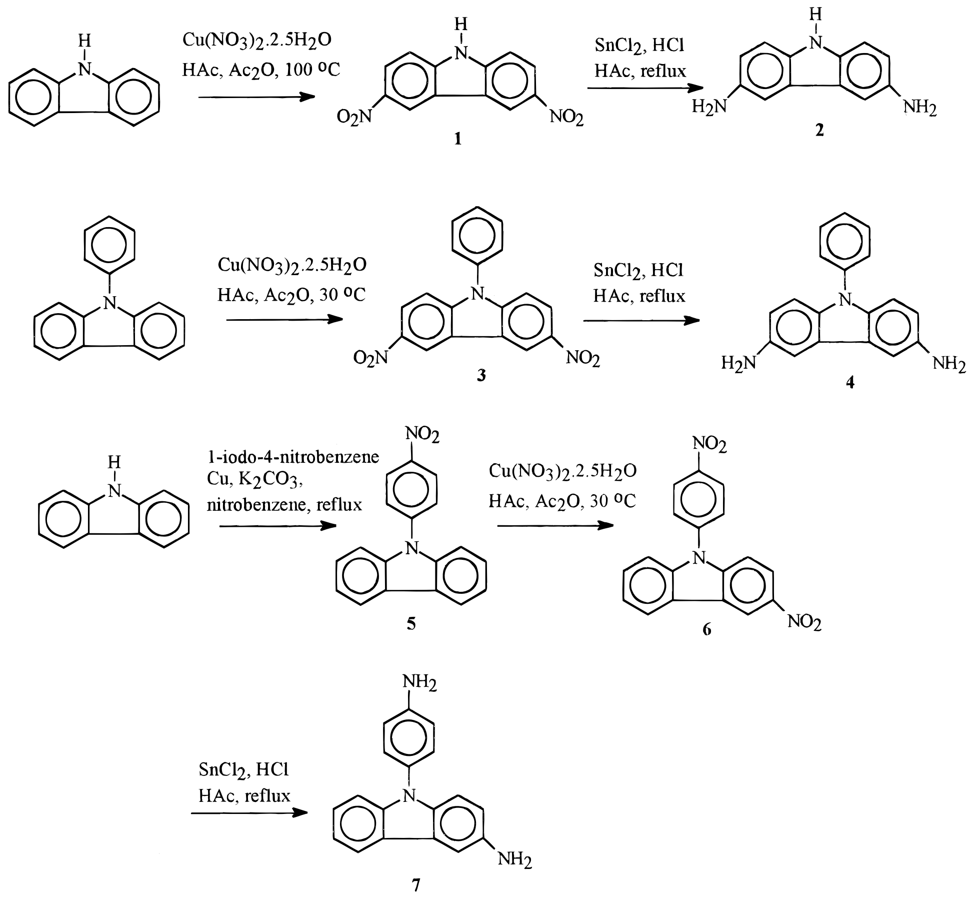
***N*-(4′-Nitrophenyl)-3-nitrocarbazole (6).** $Cu(NO_3)_2 \cdot 2.5H_2O$ (3.0 g, 13 mmol) was dissolved in a mixture of acetic acid (7.5 mL) and acetic anhydride (15 mL) at room temperature. To this solution was then added compound **5** (3.10 g, 10.8 mmol) in several portions. The reaction temperature was controlled at around 30 °C by using a water bath. The mixture was stirred at this temperature for 10 min and then poured into distilled water (200 mL). The precipitate was collected by filtration, washed with water (300 mL × 3) and air-dried. The product was purified by recrystallization from 1,2-dichlorobenzene. The yield was 2.86 g (80%): mp 231 °C (dec, DSC in air); IR (KBr) 1670, 1590, 1519, 1493, 1467, 1337, 1274, 1225, 1163, 1105, 832, 753, 694 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.06 (d, 1H, $J = 2.2$ Hz), 8.53 (d, 2H, $J = 9.0$ Hz), 8.35 (dd, 1H, $J = 9.0$ Hz, $J = 2.2$ Hz), 8.21 (d, 1H, $J = 8.5$ Hz), 7.78 (d, 2H, $J = 9.0$ Hz), 7.4−7.6 (m, 4H); MS (EI, *m*/*e*, % relative intensity) 333 (M^+, 78).

***N*-(4′-Aminophenyl)-3-aminocarbazole (7).** Compound **6** (1.80 g, 5.40 mmol) and $SnCl_2$ (18 g, 95 mmol) were placed into a round-bottomed flask, along with acetic acid (60 mL) and concentrated hydrochloric acid (10 mL). The solution was refluxed under argon for 24 h. The resulting clear solution was cooled to room temperature and then poured into an aqueous sodium hydroxide solution (20%, 500 mL). The precipitate was collected by filtration and washed with water. The product was extracted with THF, and the solution was dried over $MgSO_4$ and filtrated. Removal of the solvent afforded a light-yellow solid. It was further purified through a chromatography silica gel column eluted with acetone/hexane (1:2, v/v) and recrystallized from water/2-propanol (1:1 v/v) under argon: 0.60 g (40%); mp 181 °C (dec, DSC in air); IR (KBr) 3342, 3212, 1622, 1519, 1487, 1458, 1232, 746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, 1H, H_5, $J = 7.7$ Hz), 7.25−7.35 (m, 2H, $H_{4,6}$), 7.06−7.20 (m, 4H, $H_{7,8,3',5'}$), 6.99 (d, 1H, H_1, $J = 9.2$ Hz), 6.72−6.80 (m, 3H, $H_{2,2',6'}$), 5.34 (s, br, 2H, NH_2), 4.78 (s, br, 2H, NH_2); UV−vis (THF, λ_{max}) 310, 370 nm; MS (EI, *m*/*e*, % relative intensity) 273 (M^+, 100).

Anal. Calcd for $C_{18}H_{15}N_3$: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.07; H, 5.50; N, 14.88.

Polymerization. Polyimide 8. Diamine **2** (473 mg, 2.40 mmol) was dissolved into 15 mL of NMP. To this was added 6FDA (1065 mg, 2.40 mmol) and an additional 5 mL of NMP. The solution was stirred at room temperature under argon for

Scheme 1. Synthesis of Diamines 2, 4, and 7



24 h, yielding a viscous polyamic acid solution. To the above solution were added 2 mL of acetic anhydride and 1 mL of pyridine. The stirring was continued for 6 h at room temperature and 6 h at 60 °C. The mixture was then poured into methanol (500 mL). The precipitate was collected by filtration. The polymer was redissolved into a small amount of THF (10 mL) and reprecipitated from methanol (500 mL). The precipitate was filtrated and dried at 120 °C under high vacuum overnight: IR (KBr) 3406, 1783, 1723, 1498, 1374, 719 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1H, NH), 8.20 (d, 2H), 8.17 (s, 2H), 7.98 (d, 2H), 7.80 (s, 2H), 7.63 (d, 2H), 7.45 (d, 2H); UV−vis (THF, λ_{max}) 318 nm (shoulder), 302 nm.

Polyimide 9. Polyimide **9** was synthesized from polymerization of 1 equiv of diamine **4** and 1 equiv of 6FDA: IR (KBr) 1783, 1724, 1492, 721 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.15 (s, br, 2H), 8.05 (d, br, 2H), 7.97 (s, br, 2H), 7.89 (d, br, 2H), 7.59 (d, br, 2H), 7.53 (d, br, 2H), 7.49 (d, br, 3H), 7.43 (d, br, 2H); UV−vis (THF, λ_{max}) 318 nm (shoulder), 302 nm; T_g 400 °C and T_{dec}(onset) 469 °C in air.

Polyimide 10. Polyimide **10** was synthesized as above from 1 equiv of diamine **7** and 1 equiv of 6FDA: IR (KBr) 1789, 1724, 1516, 1457, 721 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, br, 1H), 8.08 (m, 3H), 8.00 (s, br, 1H), 7.96 (s, br, 1H), 7.93 (d, br, 2H), 7.70 (s, br, 4H), 7.59 (d, br, 1H), 7.45 (m, 3H), 7.30 (s, br, 1H); UV−vis (THF, λ_{max}) 342 nm (shoulder), 300 nm.

Polyimide 11. Polyimide **11** was synthesized as above from 1 equiv of diamine DDE and 1 equiv of 6FDA: IR (KBr) 1785, 1724 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.03 (d, br, 2H), 7.89 (m, 3H), 7.40 (d, br, 4H), 7.21 (d, br, 4H); UV−vis (THF, λ_{max}) 300 nm.

Copolyimide 12. Copolyimide **12** was synthesized from polymerization of 3 equiv of diamine **2**, 1 equiv of diamine DDE, and 4 equiv of 6FDA: IR (KBr) 3412, 1783, 1725, 1500, 1300, 722 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 11.20 (s, NH), 7.2−8.2 (m, aromatic protons); UV−vis (THF, λ_{max}) 324 nm (shoulder), 298 nm.

Copolyimide 13. Copolyimide **13** was synthesized as above from 1 equiv of diamine **2**, 1 equiv of diamine DDE, and 2 equiv of 6FDA: IR (KBr) 3412, 1783, 1727, 1501, 1375, 1246, 722 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 11.20 (s, NH), 7.2−8.2 (m, aromatic protons); UV−vis (THF, λ_{max}) 318 nm (shoulder), 300 nm.

Copolyimide 14. Copolyimide **14** was synthesized as above from 3 equiv of diamine **4**, 1 equiv of diamine DDE, and 4 equiv of 6FDA: IR (KBr) 1783, 1726, 1501, 722 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.2−8.4 (m, aromatic protons); UV−vis (THF, λ_{max}) 330 nm (shoulder), 300 nm.

Copolyimide 15. Copolyimide **15** was synthesized as above from 1 equiv of diamine **4**, 1 equiv of diamine DDE, and 2 equiv of 6FDA: IR (KBr) 1783, 1727, 1501, 1374, 722 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.2−8.4 (m, aromatic protons); UV−vis (THF, λ_{max}) 318 nm (shoulder), 300 nm.

Copolyimide 16. Copolyimide **16** was synthesized as above from 3 equiv of diamine **7**, 1 equiv of diamine DDE, and 4 equiv of 6FDA: IR (KBr) 1789, 1725, 1516, 722 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.2−8.2 (m, aromatic protons); UV−vis (THF, λ_{max}) 342 nm (shoulder), 302 nm.

Copolyimide 17. Copolyimide **17** was synthesized as above from 1 equiv of diamine **7**, 1 equiv of diamine DDE, and 2 equiv of 6FDA: IR (KBr) 1783, 1726, 1500, 1376, 722 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.2−8.2 (m, aromatic protons); UV−vis (THF, λ_{max}) 342 nm (shoulder), 302 nm.

Results and Discussion

Monomer Synthesis. Carbazole compounds have electrodonating properties, thereby allowing facile electrophilic substitution reactions, mainly at the 3 and 6 positions.[18] Carbazole compounds can be difunctionalized under appropriate conditions. In this study, three aromatic carbazole diamines, symmetric **2** and **4** and asymmetric **7**, were synthesized, and the synthetic routines are outlined in Scheme 1.

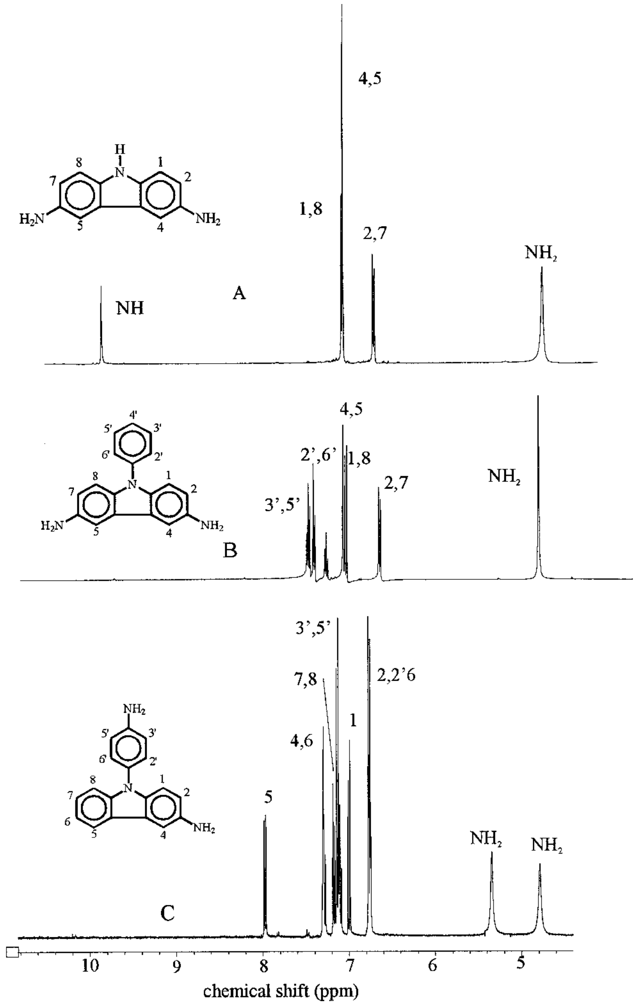
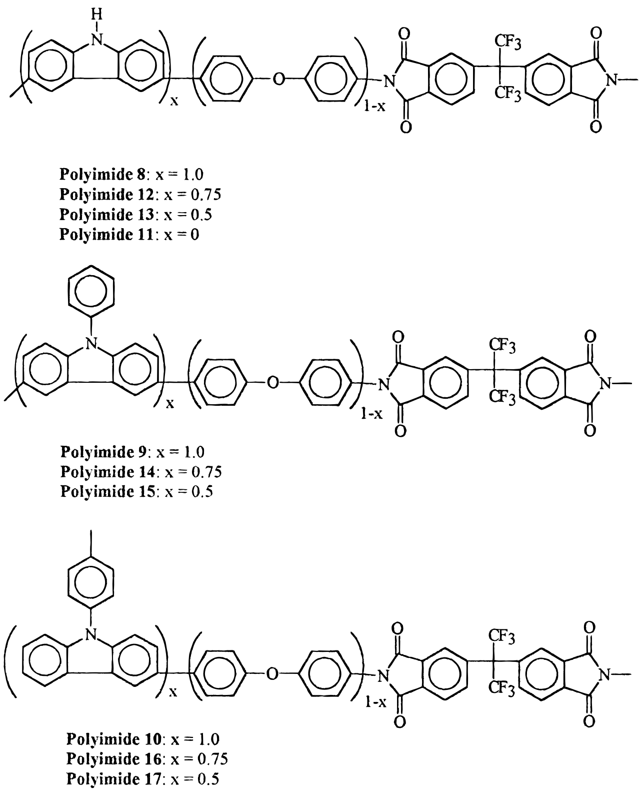


Figure 1. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of diamines **2** (A), **4** (B) and **7** (C).

As reported, carbazole can be mononitrated at the 3 position under a nitrating reagent, $Cu(NO_3)_2$, in a mixture of acetic acid and acetic anhydride at 30 °C.[28] We found that by control of the reaction temperature at around 100 °C, a dinitrated compound, 3,6-dinitrocarbazole (**1**), could be easily obtained in a good yield. NMR spectra and mass spectrum have confirmed its structure. Thus, subsequent reduction of the dinitro compound **1** with $SnCl_2$ in a mixture of hydrochloric acid and acetic acid at refluxing temperature could readily give diamine compound **2**. Again, ^{1}H NMR (Figure 1A) confirms the structure of diamine **2**. By using the similar nitration reaction condition at 30 °C, another dinitrated compound, 3,6-dinitro-*N*-phenylcarbazole (**3**), was synthesized from *N*-phenylcarbazole. This dinitration reaction should be controlled at a mild temperature, because both 3 and 6 positions are highly reactive toward electrophilic reaction due to the strong electron-donating effects from both the *N*-phenyl group and the carbazole core itself. Similarly, diamine **4** (Figure 1B) was then obtained from compound **3** by reduction. It was also reported that *N*-phenylcarbazole can be obtained from the condensation of carbazole and iodobenzene catalyzed by copper powder in a classic Ullmann reaction condition.[29] Thus, by a similar method, *N*-(4-nitrophenyl)carbazole (**5**) was prepared from the condensation of carbazole and 1-iodo-4-nitrobenzene in a moderate yield. Nitration of this compound with a mixture of $Cu(NO_3)_2$, acetic acid, and acetic anhydride at 30 °C occurred exclusively at the 3 position to afford compound **6**. Compound **6** again could be easily reduced with $SnCl_2$ to give diamine compound **7** (Figure 1C).

Chart 1. Structures of (Co)polyimides



Polyimide 8: x = 1.0
Polyimide 12: x = 0.75
Polyimide 13: x = 0.5
Polyimide 11: x = 0

Polyimide 9: x = 1.0
Polyimide 14: x = 0.75
Polyimide 15: x = 0.5

Polyimide 10: x = 1.0
Polyimide 16: x = 0.75
Polyimide 17: x = 0.5

Diamines **2** and **4** and diamine **7** have rather different structures, the former two are symmetric, while the latter is asymmetric. As can be seen from ^{1}H NMR spectra (Figure 1C), diamine **7** has two broad singlet peaks (4.78 and 5.34 ppm, respectively) from its amino protons, because of their chemical and magnetic nonequivalence. These three diamines showed blue fluorescence under UV light (254 nm) and had two maximum absorptions at around 320 and 380 nm in UV−vis spectra, due to the π-π^* transitions in the conjugated carbazole rings. DSC analyses indicated that diamine **4** displayed a sharp melting point at 157 °C. Diamines **2** and **7** did not show any melting point, but rather started to decompose at 255 °C and 181 °C, respectively.

Polyimide Synthesis and Characterization. In general, polyimide can be synthesized from condensation of a diamine and a dianhydride through either a two-step low-temperature polymerization, that is, the formation of a polyamic acid and then thermal or chemical imidization to polyimide, or a direct one-step solution polycondensation at high temperature. The former approach was adopted to synthesize polyimides in this study. As diamines **2**, **4**, and **7** are light- and air-sensitive, i.e., they oxidize easily in air, the freshly prepared or freshly recrystallized diamines were used for polymerization in order to obtain polyimides with high molecular weights. Homopolymerizations of these three diamines with a dianhydride (6FDA) were carried out in NMP at room temperature. Such condensation reactions first formed polyamic acids, and subsequent addition of acetic anhydride and pyridine caused chemical imidizations and gave polyimides in quantitative yields. Also, random copolyimides were obtained from carbazole diamines, **2**, **4**, and **7**, with a diamine DDE in

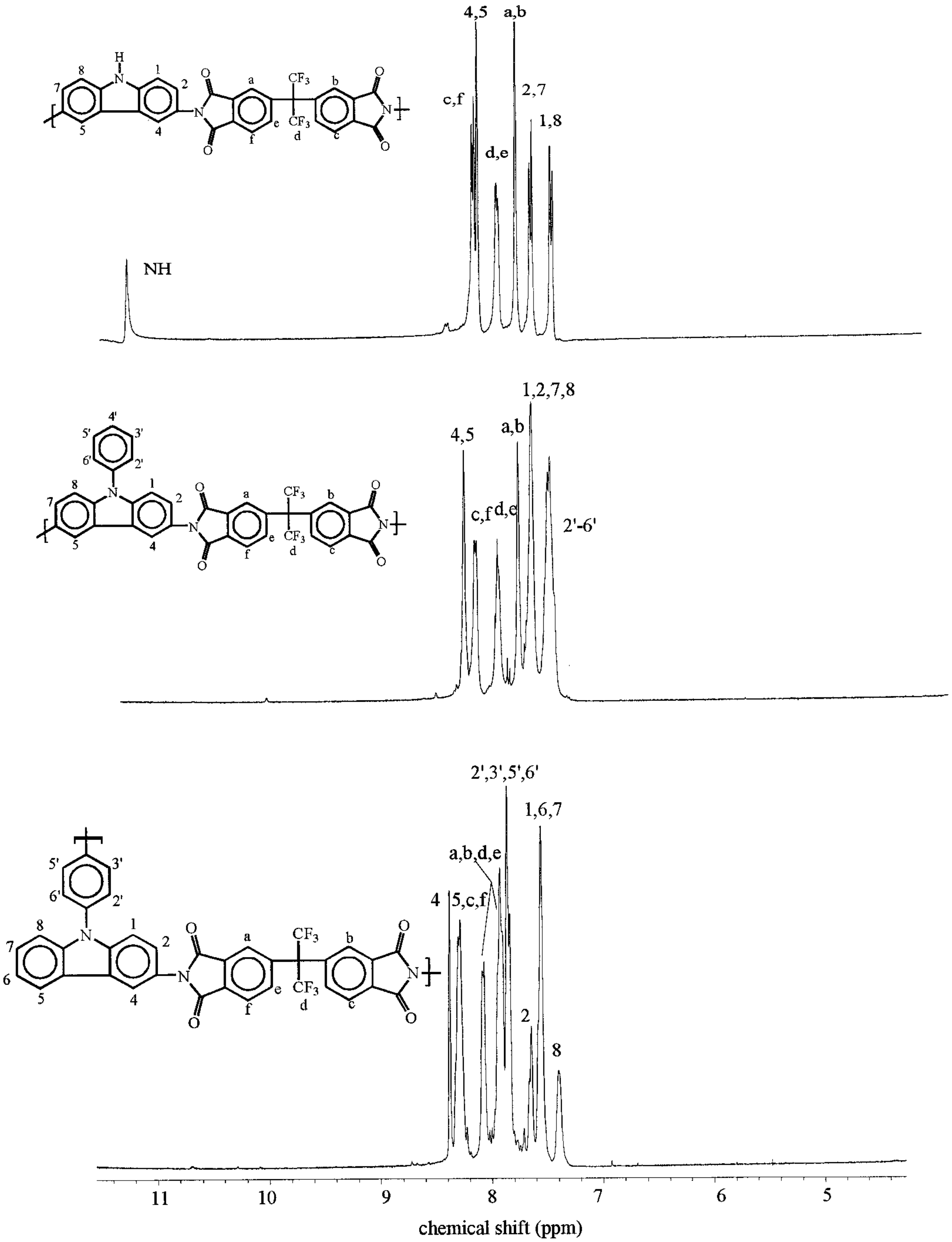


Figure 2. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of polyimides **8** (top), **9** (middle), and **10** (bottom), in the aromatic regions.

different diamine monomer molar ratios ranging from 3:1 to 1:1. In all cases, the polymerization solutions remained homogeneous when solid contents were kept at around 10 wt % or lower, thus making high molecular weight polymer possible. Chart 1 shows the structures of these polymers.

FTIR spectra of these polyimides showed imide carbonyl peaks, typically at around 1783 and 1724 cm^{-1}, and did not show amide-carbonyl peak at 1650 cm^{-1}, indicating the complete imidization during polycondensation. It is also noted from the IR spectra that a broad peak is observed at around 3424 cm^{-1} for (co)polyimides **8**, **12**, and **13**, derived from monomer **2**, indicating that the N−H amino groups at the 9 position from carbazole units remained intact during polymerizations. The characteristic NH absorbance was confirmed in the ^{1}H NMR spectrum. As can be seen from Figure 2A for polyimide **8**, a broad singlet at 11.23 ppm is observed, clearly being assigned as the amino proton on the 9 position of carbazole unit. Parts B and C of Figure 2 also show the ^{1}H NMR spectra in the aromatic regions for homopolyimides **9** and **10**. The assignments for these homopolyimides were based on 2D-COSY experiments, in good agreement with the proposed polymer structures. The compositions for other copolyimides were calculated based on ^{1}H NMR spectra integration, nearly equal to their respective monomer feeds due to the quantitative yields of the polymerizations.

All (co)polyimides exhibited maximum UV−vis absorption at around 300 nm in THF solutions, due to the $\pi-\pi^*$ transitions of the aromatic chromophores, e.g., carbazole units and phenyl rings. Polyimides containing carbazole chromophores showed an additional shoulder peak at around 320 or 340 nm, characteristic of $\pi-\pi^*$

Table 1. Solubilities of (Co)polyimides[a]

polymer	diamine(s) (mol ratio)	NMP	DMSO	DMF	*m*-cresol	THF	$CHCl_3$	CH_3OH	hexane
8	**2**	++	++	++	++	++	– –	– –	– –
9	**4**	++	++	++	++	++	++	– –	– –
10	**7**	++	++	++	++	++	++	– –	– –
11	**DDE**	++	++	++	++	++	++	– –	– –
12	**2/DDE**(3:1)	++	++	++	++	++	– –	– –	– –
13	**2/DDE**(1:1)	++	++	++	++	++	– –	– –	– –
14	**4/DDE**(3:1)	++	++	++	++	++	– –	– –	– –
15	**4/DDE**(1:1)	++	++	++	++	++	– –	– –	– –
16	**7/DDE**(3:1)	++	++	++	++	++	– –	– –	– –
17	**7/DDE**(1:1)	++	++	++	++	++	– –	– –	– –

[a] Solubility: ++, soluble at room temperature; – –, insoluble at room temperature.

Table 2. Properties of (Co)polyimides

(co)polyimide	diamine(s) (molar ratio)	M_w[a] ($\times 10^{-4}$)	PDI[a]	T_g (°C)[b]	T_d (°C)[b]	λ_{max} (nm)[c]
8	2	4.2	2.0		356	302, 318 (sh)
9	4	5.9	1.9	400	473	302, 318 (sh)
10	7	1.5	1.5		431	300, 342 (sh)
11	DDE	9.8	1.7	295	414	300
12	2/**DDE**(3:1)	3.3	2.1		341	298, 324 (sh)
13	2/**DDE**(1:1)	5.7	2.4		340	300, 318 (sh)
14	4/**DDE**(3:1)	5.0	2.0	365	472	300, 330 (sh)
15	4/**DDE**(1:1)	4.4	2.4	341	397	300, 318 (sh)
16	7/**DDE**(3:1)	2.3	1.8		412	302, 342 (sh)
17	7/**DDE**(1:)	5.0	2.2		431	302, 342 (sh)

[a] GPC analysis, relative to polystyrene standards. [b] DSC analysis at a heating of 10 °C/min in air. [c] UV/vis measurements in THF at room temperature. sh: shoulder.

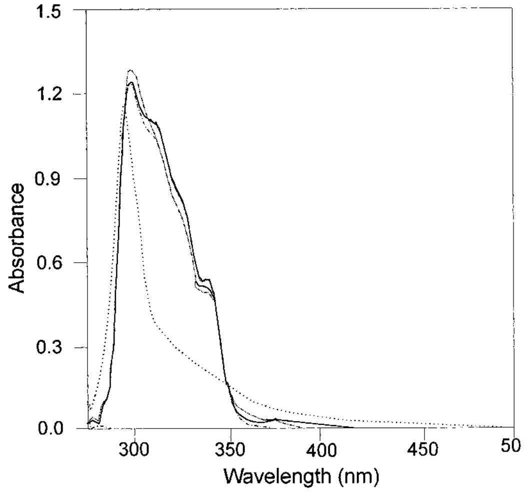


Figure 3. UV–vis spectra of (co)polyimides **9** (—), **11** (···), **14** (– · –), and **15** (– · · –) in THF at room temperature.

transitions of carbazole molecules. Figure 3 shows the UV–vis spectra of (co)polyimides **10**, **11**, **16**, and **17**. Polymers **10**, **16** and **17** have identical spectra. Polymer **11** is different, because it does not contain any carbazole. It seems that the polymer composition, such as carbazole chromophore content in these polymer systems, did not significantly affect the UV–vis absorptions. This suggests that these three (co)polyimides have similar conjugated carbazole length. Similar results have also been observed for the other carbazole-containing (co)polyimides.

The solubilities of these polymers were tested in various solvents (Table 1). It was found that (co)polyimides derived from diamines **4** and **7** were readily soluble in organic solvents, such as chloroform, THF, DMF, DMSO, NMP, and *m*-cresol. The pendent *N*-phenyl groups in the carbazole unit for (co)polyimides derived from diamines **4** reduce the rigidity and enhance the flexibility along polymer main chains, thus resulting in good polymer solubility. On the other hand, due to the asymmetric nature of diamine **7**, polyimides derived from this monomer have two possible different diads, namely, head to head, and head to tail. The NMR spectrum is too complicated, and different linkages of these type cannot be identified there. These head-to-head and head-to-tail linkages should be the main reason for the improved solubility in these polymer systems. In a comparison, although (co)polyimides **8**, **12**, and **13** derived from monomer **2** can also be soluble in THF, DMF, DMSO, NMP, and *m*-cresol, they were insoluble in chloroform and dichlormethane, probably due to the lack of flexible group in the carbazole cores and also the possible hydrogen bonding between the free amino groups.

The weight-average molecular weights (M_w) of these polymers estimated by GPC ranged from 1.5×10^4 to 5.9×10^4, relative to standard polystyrene, and the polydispersity index (PDI) was from 1.5 to 2.4. As can be seen from Table 2, polyimide **10** from monomer **7** has a relatively low molecular weight. This is due to the fact that monomer **7** has two different amino groups as mentioned above (Figure 1C), which should have different reactivities toward the anhydride groups of 6FDA.

Regarding thermal properties, (co)polyimides derived from diamines **2** and **7** did not show any glass transition temperatures (T_gs) prior to thermal decomposition in air, because of their rigid polymer backbones. T_gs, however, can be detected from (co)polyimides derived from monomer **4**. This is probably due to the existence of the *N*-phenyl groups on the carbazole units, which decrease the ability for facile chain packing and thus enhance the polymer chain mobility. Polyimide **9** has a very high T_g at 400 °C, and T_gs increase in the following order of polymer, **9** > **14** > **15** > **11**, as a consequence of decreasing the carbazole monomer content in polymer compositions. The onset decomposition temperature (T_d), a parameter for the thermal stability, of these polymers also evaluated from DSC experiments was from 356 to 473 °C. Their different thermal stabilities are related with the polymer compositions and carbazole monomeric structures. The (co)polyimides derived from monomers **4** and **7** have fairly high thermal stability. In a comparison, (co)polyimides derived from monomer **2** have relatively low T_ds (356 °C for **8**, 341 °C for **12**, and 340 °C for **13**), due to the amino group's thermooxidative sensitivity to air.

Conclusions

Three new carbazole-based aromatic diamines were synthesized in moderate yields. Two-step polycondensation of these three diamines and DDE with 6FDA produced soluble (co)polyimides, having weight-average molecular weights of 1.5×10^4 to 5.9×10^4. Thus, carbazole units were successfully incorporated into polyimides main chains. These polyimides were characterized by solution NMR, IR, UV−vis, and DSC.

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