

# Synthesis and Characterization of Imine-Coupled Polyphenols Containing Carbazole Units

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**ABSTRACT:** Imine coupled phenolic monomers containing carbazole unit were synthesized in four steps. The monomers were polymerized via oxidative polycondensation by air as oxidant in an aqueous alkaline medium at 50°C. The structures of compounds were confirmed by ultraviolet-visible (UV-vis), Fourier transform infrared, and <sup>1</sup>H- and <sup>13</sup>C-NMR techniques. The conductivity measurements of these polymers were made by the four-point probe technique and iodine was used as doping agent. The highest occupied molecular orbital, the lowest unoccupied molecular orbital, and electrochemical and optical band gap values were calculated by the results of the UV-

vis and the cyclic voltammetry measurement, respectively. The number-average molecular weight, weight-average molecular weight, and polydispersity index values were determined by the size exclusion chromatography technique. Also, thermal behavior of these polymers was determined by thermogravimetric/differential thermal analysis measurements in a N<sub>2</sub> atmosphere between 20 and 1000°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1975–1985, 2009

**Key words:** oxidative polycondensation; carbazole; band gap; polyphenols; thermal properties

## INTRODUCTION

Usually oligo- or polyphenols have been synthesized via oxidative polycondensation reactions by using oxidants such as sodium hypochlorite (NaOCl), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and air in an aqueous alkaline medium at the various reaction temperatures and times.<sup>1–3</sup> Imine (–CH=N) coupled oligo- or polyphenols have useful properties such as paramagnetism, semiconductivity, electrochemical cells, and resistance to high energy.<sup>2,4</sup> The –CH=N is iso-electronic with the CH=CH in the structures of these polymers. The incorporation of nitrogen atoms into the conjugated system is another approach to develop material classes with interesting electronic and optical properties.<sup>5</sup> Because of these properties, they can be used to prepare composites with resistance to high temperature, thermostabilizations and graphite materials, epoxy polymer and block copolymer adhesives, photoresists, and antistatic materials.<sup>6–10</sup> Also these polymers have become an increasingly interesting area of semiconducting and optical materials. These materials possess great potential for device applications such as light-emitting diodes, thin film transistors, and photovoltaic cells.<sup>11,12</sup>

Activity related to photoconductivity in carbazole-containing polymers<sup>13–15</sup> originated with the discovery of photoconductivity in poly(*N*-vinylcarbazole)

by Hoegl.<sup>16</sup> They constituted an important part of photoconductive polymers. Much attention was paid to carbazole-based compounds in the studies of photoconductive polymers and organic photoreceptors.<sup>17</sup> Due to properties, such as ease of formation, relatively stable radical cations (holes), high charge carrier mobilities, high thermal and photochemical stability, carbazole-containing polymers are useful as electrical semiconductors, nonlinear optical devices, polymer light emission devices, solar cells, and electrochromic or smart windows.<sup>18,19</sup> From a structural point of view, carbazole differs from diphenylamine in its planar structure, and the bonded diphenylamine implies higher thermal stability of such carbazole-containing materials. Also, carbazole can be easily functionalized at the (3,6),<sup>20,21</sup> (2,7),<sup>22</sup> or N positions<sup>23</sup> and then covalently links into polymeric systems, both in the main chain<sup>24</sup> as building blocks and in a side chain as pendent groups.<sup>25</sup>

In this article, we report on polyphenols containing carbazole units synthesized via oxidative polycondensation reaction by using air. Electrochemical and optical band gaps of monomers and polymers were calculated from the results of cyclic voltammetry (CV) and ultraviolet-visible (UV-vis) spectroscopy. Conductivity measurements were carried out by an electrometer by using the four-point probe technique. Also, size exclusion chromatography (SEC) and thermogravimetric/differential thermal analyzer (TG-DTA) techniques were used for determination of molecular weight and thermal behavior of the synthesized compounds, respectively.

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## MATERIALS AND METHODS

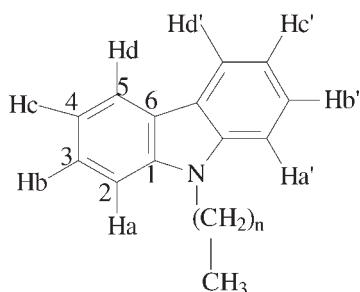
### Materials

Carbazole, 4-hydroxybenzaldehyde, 1-bromoethane, 1-bromobutane, 1-bromohexane, 1-bromododecane, and tetrabutylammoniumhexafluorophosphate (TBAPF<sub>6</sub>) were supplied from Fluka. Dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol (MeOH), chloroform (CHCl<sub>3</sub>), acetonitrile (CH<sub>3</sub>CN), toluene, and tetrahydrofuran used as solvent were supplied from Merck Chemical (Germany). Acetic anhydride, acetic acid (CH<sub>3</sub>COOH), potassium hydroxide (KOH), copper(II) nitratehemipentahydrate [Cu(NO<sub>3</sub>)<sub>2</sub> × 2.5H<sub>2</sub>O], 18-Crown-6, and palladium on activated carbon (Pd/C) (10% w/w) were also supplied from Merck Chemical (Darmstadt, Germany).

### Synthesis of 9-*N*-alkylcarbazole (9-NAC)

Carbazole (10 mmol) and KOH (15 mmol) were added to 20 mL toluene and refluxed for 30 min. 18-Crown-6 (0.01 mL) was used as phase transfer catalysis in the reaction medium. The solution of 1-bromoalkane (1-bromoethane, 1-bromobutane, 1-bromohexane, 1-bromododecane) (15 mmol) compounds in 10 mL toluene was slowly added to the reaction mixture. The mixture was stirred at 110°C for 6 h and then cooled to room temperature. Then, the reaction mixture was poured into the 150 mL ethanol and stripped off by a rotary evaporator. The product was recrystallized from methanol and dried in vacuum desiccators. Yield: 9-*N*-ethyl-carb: 88%; 9-*N*-butyl-carb: 84%, 9-*N*-hexyl-carb: 76%, 9-*N*-dodecyl-carb: 54%.

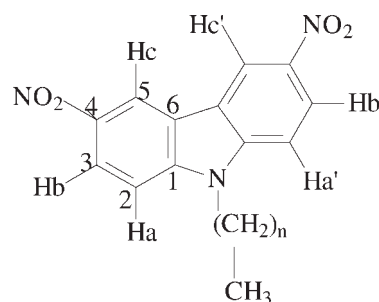
UV-vis ( $\beta_{\max}$ ) (MeOH): 236, 261, 233, and 330 nm. FTIR (cm<sup>-1</sup>): (C—H aromatic) 3048; (C—H aliphatic) 2911, 2845; (C=C phenyl) 1593, 1484, 1451; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 8.16 (s, (d, 2H, Ar—H<sub>aa'</sub>); 7.65 (d, 2H, Ar—H<sub>dd'</sub>); 7.55 (t, 2H, Ar—H<sub>bb'</sub>); 7.28 (s, 2H, H<sub>cc'</sub>); 4.38 (t, 2H, —N—CH<sub>2</sub>—); 1.94–1.27 (CH aliphatic; for butyl-Carb, *N*-Hexyl-Carb, *N*-Dodecyl-Carb), 0.92 (d, 3H, R-CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 141 (C1); 108 (C2); 126 (C3); 117 (C4); 119 (C5); 123 (C6); 44 (N—CH<sub>2</sub>); 34–21 (N—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>n</sub>); 14 (CH<sub>2</sub>—CH<sub>3</sub>).



### Synthesis of 3,6-dinitro-9-*N*-alkylcarbazole (3,6-DN-9-NAC)

Cu(NO<sub>3</sub>)<sub>2</sub> × 2.5H<sub>2</sub>O (20 mmol) was added to a mixture of acetic acid (15 mL) and acetic anhydride (30 mL) at room temperature. The mixture was stirred for 10 min, and then *N*-alkylcarbazole (18 mmol) was slowly added to this solution. After 5 min, 10 mL acetic acid was added to the reaction mixture. The mixture was further stirred at this temperature for 45 min and then poured into distilled water (500 mL). The yellow precipitate was collected by filtration, washed with water (300 mL × 3), and dried at 60°C under vacuum. Yield: 3,6-dinitro-*N*-ethyl-carb.: 94%; 3,6-dinitro-*N*-butyl-carb.: 96%, 3,6-dinitro-9-*N*-hexyl-carb.: 82%, 3,6-dinitro-*N*-dodecyl-carb.: 78%.

UV-vis ( $\beta_{\max}$ ) (MeOH): 230, 265, 292, and 365 nm. FTIR (cm<sup>-1</sup>): (C—H aromatic) 3090–3063; (C—H aliphatic) 2920, 2850; (—NO<sub>2</sub>), 1512, 1312; (C=C phenyl) 1601, 1473, 436. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 9.18 (s, 2H, Ar—H<sub>cc'</sub>); 8.59 (d, 2H, Ar—H<sub>bb'</sub>); 7.61 (d, 2H, Ar—H<sub>aa'</sub>); 4.41 (t, 2H, —N—CH<sub>2</sub>—); 1.94–1.22 (CH aliphatic; for butyl-Carb, *N*-Hexyl-Carb, *N*-Dodecyl-Carb), 0.92 (d, 3H, R-CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 147 (C1); 109 (C2); 127 (C3); 144 (C4); 116 (C5); 124 (C6); 43 (N—CH<sub>2</sub>); 34–21 (N—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>n</sub>); 14 (—CH<sub>2</sub>—CH<sub>3</sub>).



### Synthesis of 3,6-diamino-9-*N*-alkylcarbazole (3,6-DA-9-NAC)

Pd/C (10% w/w) (0.01 g) was added to the solution of 3,6-dinitro-9-*N*-ethyl-carbazole (15 mmol) in 200 mL ethanol at room temperature. Then the mixture was heated to reflux temperature for 10 min. Then, 10 mL hydrazinium hydroxide in 30 mL ethanol was added to the solution dropwise for 45 min. The mixture was stirred at 40°C for 24 h and then the Pd on carbon was filtered off. Ethanol was stripped by a rotary evaporator and the remaining solid was crystallized from toluene two times. The solid was dried at 50°C under vacuum. The yield of 3,6-diamino-9-*N*-ethyl-carbazole was found to be 68%.

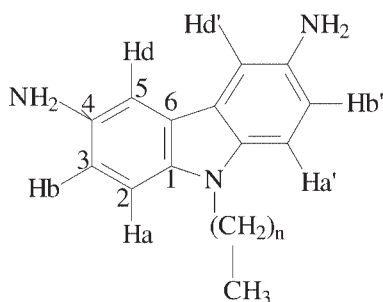
Pd/C (10% w/w) (0.01 g) was added to the solution of 3,6-dinitro-9-*N*-butyl-carbazole (15 mmol) in 200 mL ethanol at room temperature. Then the mixture was heated to reflux temperature for 10 min. Then, 10 mL hydrazinium hydroxide in 30 mL

ethanol was added to the solution dropwise for 45 min. The mixture was stirred at 40°C for 24 h and then the Pd on carbon was filtered off. Ethanol was stripped by a rotary evaporator and the remaining solid was crystallized from toluene two times. The solid was dried at 50°C under vacuum. The yield of 3,6-diamino-9-*N*-butyl-carbazole was found to be 66%.

Pd/C (10% w/w) (0.01 g) was added to the solution of 3,6-dinitro-9-*N*-hexyl-carbazole (15 mmol) in 200 mL ethanol at room temperature. Then the mixture was heated to reflux temperature for 10 min. Then, 10 mL hydrazinium hydroxide in 30 mL ethanol was added to the solution dropwise for 45 min. The mixture was stirred at 40°C for 24 h and then the Pd on carbon was filtered off. Ethanol was stripped by a rotary evaporator and the remaining solid was crystallized from toluene two times. The solid was dried at 50°C under vacuum. The yield of 3,6-diamino-9-*N*-hexyl-carbazole was found to be 62%.

Pd/C (10% w/w) (0.01 g) was added to the solution of 3,6-dinitro-9-*N*-dodesyl-carbazole (15 mmol) in 200 mL ethanol at room temperature. Then the mixture was heated to reflux temperature for 10 min. Then, 10 mL hydrazinium hydroxide in 30 mL ethanol was added to the solution dropwise for 45 min. The mixture was stirred at 40°C for 24 h and then the Pd on carbon was filtered off. Ethanol was stripped by a rotary evaporator and the remaining solid was crystallized from toluene two times. The solid was dried at 50°C under vacuum. The yield of 3,6-diamino-9-*N*-dodesyl-carbazole was found to be 58%.

UV-vis ( $\beta_{\max}$ ) (CHCl<sub>3</sub>): 232, 292, and 366 nm. FTIR (cm<sup>-1</sup>): (—NH<sub>2</sub>) 3387, 3291 (C—H aromatic) 3049, 3018; (C—H aliphatic) 2918, 2849; (C=C phenyl) 1579, 1496, 1474. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 7.41 (s, 2H, Ar—H<sub>cc'</sub>); 6.89 (d, 2H, Ar—H<sub>bb'</sub>); 7.18 (d, 2H, Ar—H<sub>aa'</sub>); 4.38 (t, 2H, —N—CH<sub>2</sub>—); 3.71 (broad, 2H, —NH<sub>2</sub>) 1.96–1.21 (C—H aliphatic; for butyl-Carb, *N*-Hexyl-Carb, *N*-Dodesyl-Carb), 0.92 (d, 3H, R-CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 147 (C1); 109 (C2); 127 (C3); 144 (C4); 116 (C5); 124 (C6); 43 (N—CH<sub>2</sub>); 34–21 (N—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>n</sub>); 14 (CH<sub>2</sub>—CH<sub>3</sub>).

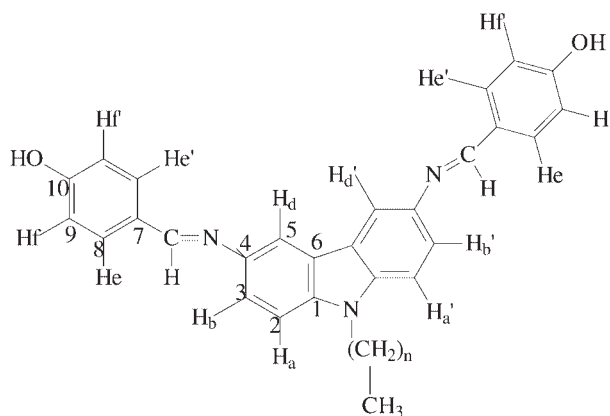


### Synthesis of phenolic monomers containing carbazole (PCs)

Phenolic monomers containing *N*-alkylcarbazole was prepared from the condensation of 4-hydroxybenzal-

dehyde (20 mmol) with 3,6-diamino-9-*N*-alkylcarbazole (10 mmol) in methanol (25 mL) achieved by boiling the mixture under reflux for 3 h. The precipitated product was filtered, recrystallized from MeOH, and dried in a vacuum desiccator. Yield: PC-1: 94%; PC-2: 88%; PC-3: 85%; PC-4: 79%.

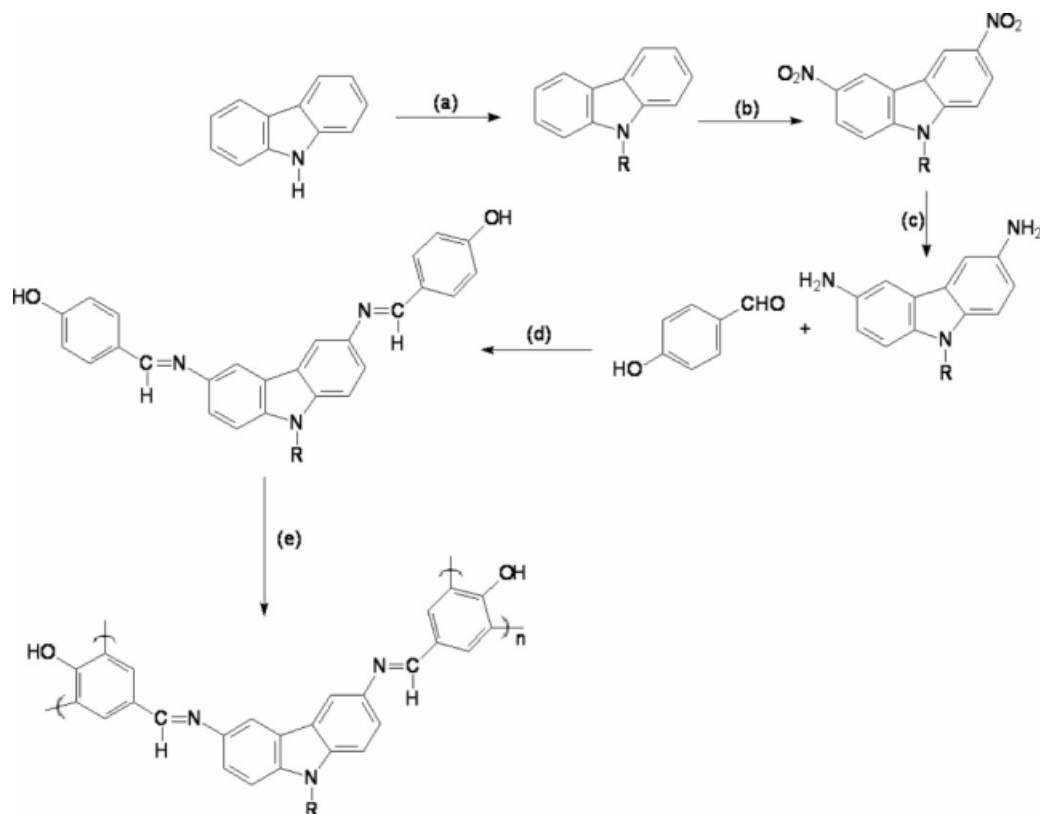
UV-vis ( $\beta_{\max}$ ) (MeOH): 222, 292, and 343 nm. FTIR (cm<sup>-1</sup>): (—OH), 3314; (C—H aromatic) 3043; (C—H aliphatic) 2972, 2932; (—CH=N—, imine), 1626; (C=C phenyl) 1596, 1583. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 10.76, (s, 2H, —OH), 8.62, (s, 2H, —CH=N—); 7.88, (d, 2H, Ar—H<sub>aa'</sub>); 7.76, (d, 2H, Ar—H<sub>cc'</sub>); 7.46 (s, 2H, Ar—H<sub>dd'</sub>); 7.32, (d, 2H, Ar—H<sub>bb'</sub>); 6.81, (d, 2H, H<sub>ff'</sub>); 4.38 (t, 2H, —N—CH<sub>2</sub>—), 1.96–1.21 [C—H aliphatic; butyl-Carb (PC-2), *N*-Hexyl-Carb (PC-3), *N*-Dodesyl-Carb (PC-4)], 0.92 (d, 3H, R-CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  ppm, 160, (—CH=N—), 142, (C1); 108, (C2); 116, (C3); 136, (C4); 121, (C5); 116, (C6); 128, (C7); 134, (C8); 118, (C9); 159, (C-10); 43, (N—CH<sub>2</sub>); 34–21, (N—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>n</sub>); 14, (CH<sub>2</sub>—CH<sub>3</sub>).



$n = 1$  (PC-1),  $n = 3$  (PC-2),  $n = 5$  (PC-3),  $n = 11$  (PC-4)

### Oxidative polycondensation of phenolic monomers containing carbazole unit

PC (5 mmol) was dissolved in an aqueous solution of KOH (10%, 10 mmol) and placed into a 50 mL three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer, and an addition of glass tubing over the condenser for air introduction. The reaction mixture was stirred at 50°C for 15 h (Scheme 1). The air was passed in at a rate of 8.5 L/h during the course of the reaction. The air passed into an aqueous solution of KOH (20%) before passage through the reaction tube to prevent water loss in the reaction mixture and remove CO<sub>2</sub>. After the completion of the reaction, the mixture was cooled to room temperature and neutralized with diluted HCl (37%, 10 mmol) at room temperature (25°C). The mixture was filtered and washed with hot water (25 mL  $\times$  3) for separating from mineral salt and then dried in an oven at 110°C. Yield: Poly-PC-1: 74%; Poly-PC-2: 68%; Poly-PC-3: 67%; Poly-PC-4: 62%.



**Scheme 1** Synthesis of imine coupled polyphenols containing carbazole unit (Poly-PC). R: C<sub>2</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>13</sub>, and C<sub>12</sub>H<sub>25</sub> (a) R-Br, KOH, 18-crown-6, toluene, 110°C, 10 h reflux, (b) Cu(NO<sub>3</sub>)<sub>2</sub> × 2.5 H<sub>2</sub>O, acetic acid–acetic anhydride, 1 h, r.t., (c) Pd/C, N<sub>2</sub>H<sub>4</sub>OH, EtOH, 24 h reflux, (d) MeOH, 3 h reflux, and (e) air, KOH, 50°C, 15 h.

UV–vis ( $\beta_{\max}$ ) (MeOH): 234, 268, 298, and 354 nm. FTIR (cm<sup>-1</sup>): 3311 (–OH), (C–H aromatic) 3053; (C–H aliphatic) 2972, 2927, 2870; (–CH=N–, imine), 1613; (C=C phenyl) 1590, 1550; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  ppm, 10.75 (broad, 2H, –OH), 8.58, (s, 2H, –CH=N–); 7.99–6.82 (m, 10H, C–H aromatic), 4.34 (t, 2H, –N–CH<sub>2</sub>–), 1.88–1.21 (m, 18H, C–H aliphatic; Poly-PC-4), 0.88 (t, 3H, R-CH<sub>3</sub>).

### Electrochemical properties

Electrochemical properties of PC and Poly-PC compounds were determined by CH Instruments 660 C

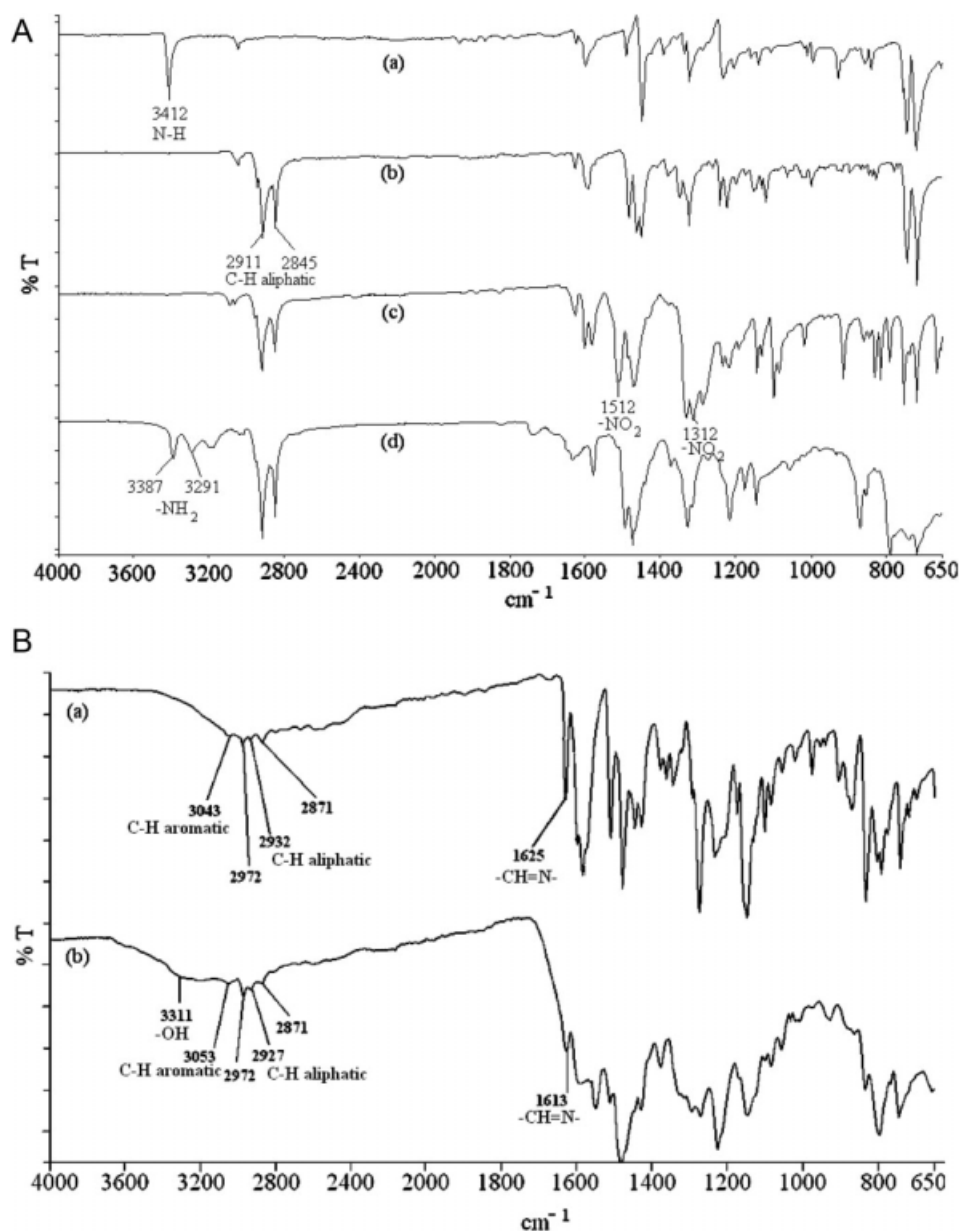
cyclic voltammetry. The electrochemical cell consists of an Ag wire as reference electrode, Pt wire as counter electrode, and glassy carbon as working electrode immersed in 0.1M TBAPF<sub>6</sub> as supporting electrolyte. The experiments were carried out under argon atmosphere. The potentials were calibrated to the ferrocene redox couple  $E^\circ(\text{Fc}/\text{Fc}^+) = +0.41$  V vs. Ag/Ag<sup>+</sup>. All reported potentials were given vs. Ag/AgCl.<sup>26</sup> The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels and electrochemical band gaps ( $E_g'$ ) of the monomers and the polymers were calculated from their oxidation and reduction onset values.

**TABLE I**  
Solubility of Synthesized Monomers and Polymers Compounds (0.05 g in 10 mL)

Compounds	NMP	DMSO	DMF	Ethyl acetate	CHCl <sub>3</sub>	Acetone	CH <sub>3</sub> OH	CH <sub>3</sub> CN	Toluene	Hexane
PC-1	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/-	-/-
PC-2	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/-	-/+
PC-3	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/-	-/+
PC-4	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/-	-/+
Poly-PC-1	+/+	+/+	+/+	+/+	+/+	+/+	-/+	+/+	-/+	-/-
Poly-PC-2	+/+	+/+	+/+	+/+	+/+	+/+	-/+	+/+	+/+	-/+
Poly-PC-3	+/+	+/+	+/+	+/+	+/+	+/+	-/+	+/+	+/-	-/+
Poly-PC-4	+/+	+/+	+/+	+/+	+/+	+/+	-/+	+/+	+/-	-/+

+/+: soluble at room temperature; -/+: soluble at heating; -/- insoluble.





**Figure 1** (A) FTIR spectra of (a) carbazole, (b) 9-NAC, (c) 3,6-DN-9-NAC, and (d) 3,6-DA-9-NAC. (B) FTIR spectra of (a) PC-3 and (b) Poly-PC-3.

### Electrical properties

Conductivity measurements were carried out by a Keithley 2400 electrometer (Keithley, OH) by using a four-point probe technique. The pellets were pressed on a hydraulic press developing up to about  $1.70 \times 10^3$  kg/cm<sup>2</sup>. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.<sup>27</sup>

### Optical properties

UV-vis spectra were measured by Perkin-Elmer Lambda 25 (MA). The absorption spectra of these compounds were recorded in a solution of MeOH.

The optical band gaps ( $E_g$ ) of the monomers and polymers were calculated from their absorption edges.<sup>28</sup>

### Solubility and characterization techniques

Solubility test results of synthesized compounds are shown in Table I. The Fourier transform infrared (FTIR) spectra were obtained by using a Perkin-Elmer FTIR Spectrum One. The FTIR spectra were recorded with an ATR attachment (4000–650 cm<sup>-1</sup>). Beginning compounds, and the monomers and the polymers were characterized by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra (Bruker Avance DPX-400 and

100.6 MHz, respectively) recorded at 25°C by using  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$ , respectively, as solvents. Tetramethylsilane was used as internal standard. Thermal data were obtained by using a Perkin-Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20 and 1000°C (in  $\text{N}_2$ , 10°C/min). The  $M_n$ ,  $M_w$ , and polydispersity index (PDI) values were determined by SEC (Shimadzu, Japan) with a Macherey-Nagel GmbH & Co. (Germany) (100 Å and 7-nm-diameter loading material) 7.7 mm i.d. × 300 mm columns, DMF/MeOH eluent (v/v, 4/1, 0.4 mL/min), polystyrene standards, and a refractive index detector at 30°C.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The oxidative polycondensation reactions of phenolic imine monomers containing *N*-alkylcarbazole was carried out by using air as oxidant in an aqueous alkaline medium at 50°C for 15 h. The yields of polymerization reaction were decreased from 74 to 62% with increasing alkyl chain length on the carbazole nitrogen. These differences might be caused by steric hindrance from the alkyl groups along the polymer.

All compounds were characterized by FTIR,  $^1\text{H}$ -, and  $^{13}\text{C}$ -NMR. There were significant changes in the

spectral properties of the initial compounds and the products. Although some of the signals disappeared, some new ones appeared in the polymer spectra. In FTIR spectra of 9-NAC derivatives, aliphatic C—H vibration was observed at 2911 and 2845  $\text{cm}^{-1}$ . Furthermore, characteristic N—H vibration at 3412  $\text{cm}^{-1}$  for secondary amines was removed by substitution with alkyl groups. In FTIR spectra of the 3,6-DN-9-NAC,  $-\text{NO}_2$  bond vibrations were observed at 1512 and 1312  $\text{cm}^{-1}$ . Also,  $-\text{NH}_2$  vibrations, resulting from reduction of the 3,6-DN-9-NAC, were clearly observed at 3387 and 3291  $\text{cm}^{-1}$  in this spectra. Finally, in FTIR spectra of PC-1, PC-2, PC-3, and PC-4 synthesized from the condensation reaction of 4-hydroxybenzaldehyde with 3,6-DA-9-NAC derivatives, the imine bond ( $-\text{CH}=\text{N}-$ ) vibration at 1625  $\text{cm}^{-1}$  was evident. Also,  $-\text{NH}_2$  bonds signals attributed to 3,6-DA-9-NAC compounds disappeared and a broad signal attributed to  $-\text{OH}$  bonds was observed at 3311  $\text{cm}^{-1}$ . After polymerization the imine bond vibration shifted to a low energy level (1613  $\text{cm}^{-1}$ ), due to presence of the conjugate  $\pi$  system at the structures of polymers. Because of the same effect, other bond vibrations were broadened and slightly shifted at the end of the polymerization. FTIR spectra of all synthesized compounds are presented in Figure 1(A,B).

Molecular structure of PC and Poly-PC compounds were also identified from their  $^1\text{H}$ - and

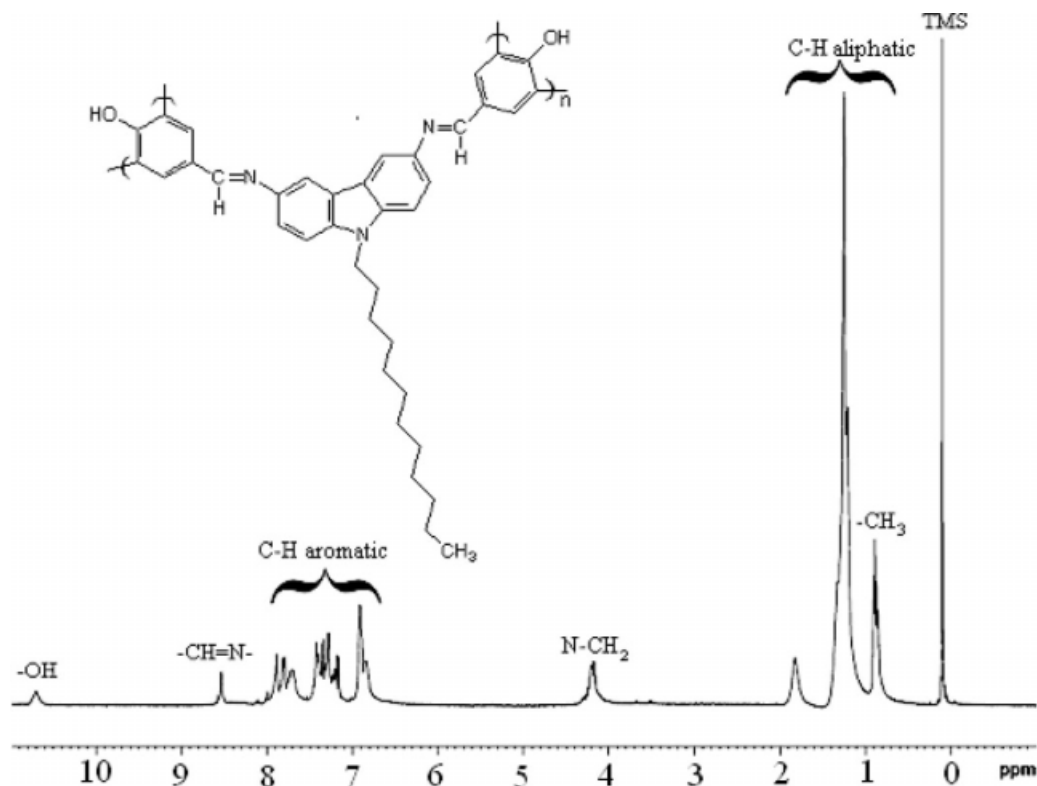


Figure 2  $^1\text{H}$ -NMR spectra of Poly-PC-4.

TABLE II  
The  $M_n$ ,  $M_w$ , and PDI Values of PC Polymers

Compounds	Molecular weight distribution parameters										
	Total			Fraction I				Fraction II			
	$M_n$	$M_w$	PDI	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%
Poly-PC-1	3,200	4,200	1.313	4,100	5,850	1.427	80	15,300	18,950	1.239	20
Poly-PC-2	4,000	4,700	1.175	6,200	7,450	1.202	82	16,400	18,200	1.110	18
Poly-PC-3	4,100	5,300	1.293	6,750	9,050	1.341	90	21,500	24,800	1.154	10
Poly-PC-4	10,750	12,300	1.144	21,100	24,350	1.154	85	23,800	25,900	1.088	15

$^{13}\text{C}$ -NMR spectra recorded in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$ , respectively. The  $^1\text{H}$ -NMR spectra of Poly-PC-4 are shown in Figure 2. While characteristic  $-\text{OH}$  and imine protons signals were observed at 10.75 and 8.89 ppm, respectively, the signals of aromatic protons were observed between 7.99 and 6.82 ppm. Because nitrogen was an electronegative atom,  $\text{N}-\text{CH}_2$  protons were observed at higher ppm than other aliphatic protons. Furthermore, a signal for  $-\text{CH}_3$  end groups was observed at 0.88 ppm as expected. At the end of the polymerization, whole proton signals broadened and slightly shifted. These results indicated that all reactions were completed successfully. According to the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR results, the polymerization of imine compounds derived from  $\text{C}-\text{C}$  and  $\text{C}-\text{O}$  coupling at the *ortho* position of  $-\text{OH}$  group and oxyphenylene, respectively.<sup>29,30</sup> According to  $^1\text{H}$ -NMR spectra of Poly-PC-4, the integral value of the hydroxyl group was found as 0.60. According to this result, the  $\text{C}-\text{C}$  and  $\text{C}-\text{O}$  coupling ratios were found to be 60 and 40%, respectively, for Poly-PC-4.

From the SEC analyses of polymers, the  $M_n$ ,  $M_w$ , and PDI values were calculated according to a polystyrene standard calibration curve and results are given in Table II. Two peaks were observed in these chromatograms of polymers. These polymers contained about 8–19 repeating units and showed narrow a molecular weight distribution. The  $M_n$ ,  $M_w$ , and PDI values of Poly-PC-1, Poly-PC-2, Poly-PC-3, and Poly-PC-4 were found to be 3200, 4200 g/mol and 1.313; 4000, 4700 g/mol and 1.175; 4100, 5300 g/mol and 1.293; 10,750, 12,300 g/mol and 1.144, respectively.

### Optical and electrochemical properties

The UV-vis absorption spectra of the monomers and polymers were recorded in MeOH solution (Fig. 3). PC monomers and polymers showed multiabsorption peaks attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the phenol, carbazole, and imine moieties. They show absorption maxima in the range of 260–315 nm and these values are attributed to characteristic of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of carbazole

and phenol moiety, respectively. The absorption at higher wavelength (360–420 nm) is attributed to  $n \rightarrow \pi^*$  transition of imine ( $-\text{CH}=\text{N}-$ ) conjugated between carbazole and phenol. Due to more extended conjugation, compared with the monomers, the absorption band of polymers broadened and slightly shifted to the low energy range. Also, Figure 3 shows that the absorption maximum ( $\lambda_{\text{max}}$ ) of Poly-PC-1 and exhibited 11 nm red shifted as compared to PC-1. While the low energy edge of the absorption spectrum of PC-1 was at 422 nm, which corresponded to a band gap ( $E_g$ ) of 2.94 eV, the low energy edge for absorption of Poly-PC-1 was at 482 nm, which corresponded to a band gap ( $E_g$ ) of 2.57 eV. Finally, electronic absorption and optical band gap values of PC the monomers and the polymers are shown in Table III.

The electrochemical properties of PC monomers and polymers were investigated by cyclic voltammetry. The cyclic voltammograms of the PC-1 and Poly-PC-1 are given in Figure 4. The cyclic voltammetry measurements of PC-1 and Poly-PC-1 were carried out in  $\text{CH}_3\text{CN}$  solution at room temperature and by using 0.1M TBAPF<sub>6</sub> as supporting electrolyte. In the cathodic scan region, PC and Poly-PC compounds exhibited only one semireversible peak between 2.08 and 2.14 V, which reflected the reduction of imine ( $-\text{CH}=\text{N}-$ ) (Scheme 2). Due to the

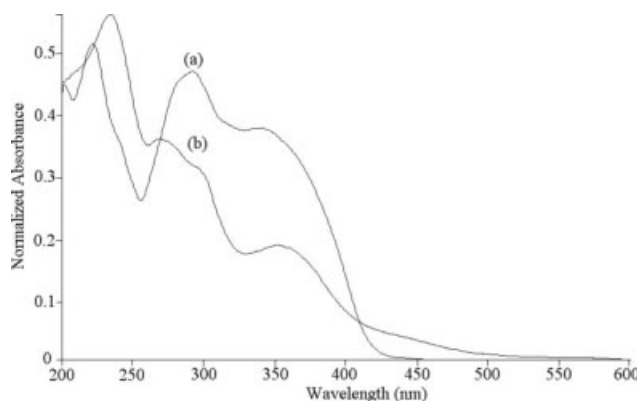


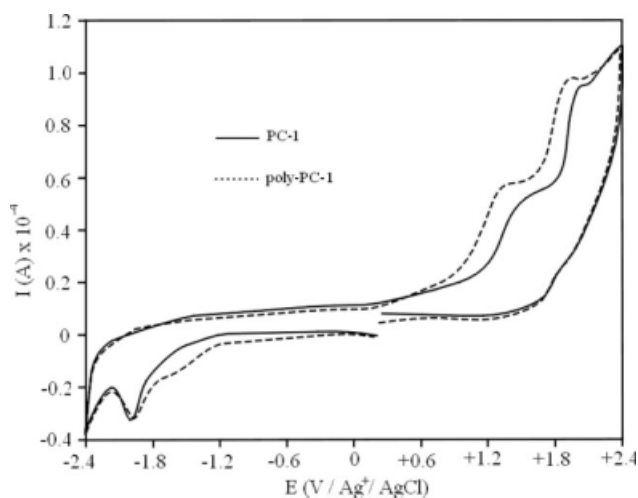
Figure 3 Absorption spectra of PC-1 (a) and Poly-PC-1 (b) in methanol solution.

**TABLE III**  
**HOMO-LUMO Energy Levels, Electrochemical, ( $E_g'$ ), and Optical ( $E_g$ ) Band Gaps Values of PC and Poly-PC Compounds**

Compounds	Reduced groups and peak potentials (V)	Oxidized groups and peak potentials (V)		HOMO (eV)	LUMO (eV)	$(E_g')$ , Electrochemical band gap (eV)	$(E_g)$ , Optical band gap (eV)
	—HC=N—(imine)	Carbazole (ring)	Phenol (ring)				
PC-1	2.08	1.64	2.11	-5.67	-2.51	3.16	2.94
PC-2	2.08	1.64	2.11	-5.67	-2.51	3.16	2.94
PC-3	2.09	1.64	2.11	-5.67	-2.51	3.16	2.94
PC-4	2.14	1.64	2.11	-5.67	-2.48	3.19	2.94
Poly-PC-1	2.02	1.42	1.94	-5.43	-2.60	2.83	2.57
Poly-PC-2	2.02	1.42	1.95	-5.43	-2.60	2.83	2.57
Poly-PC-3	2.02	1.45	1.98	-5.45	-2.60	2.85	2.57
Poly-PC-4	2.08	1.52	2.02	-5.48	-2.54	2.94	2.57

reduction potential values being sensitive to intramolecular and intermolecular electron transfer, imine reduction peaks were influenced by alkyl groups on the carbozyl nitrogen. For this reason, the reduction peak was shifted to lower potential by increasing the alkyl chain and also the band gap increased. On the other hand, due to more extended conjugation, the peak was broadened and slightly shifted to a higher potential level at the end of the polymerization. The reaction mechanism can be proposed as shown in Scheme 2.

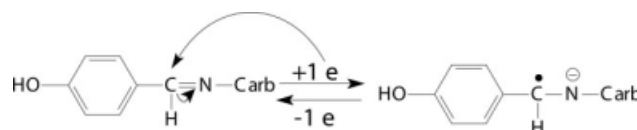
During the anodic scan of whole PC monomers two irreversible oxidation waves were observed (Fig. 4). For PC-1, the first oxidation peak at +1.64 V could be attributed to carbazole oxidation and the second one at +2.11 V could be attributed to phenolic oxidation.<sup>31</sup> However, in the CV measurements of Poly-PC-1, the carbazole and phenolic oxidation shifted to lower potential because of the extended conjugation in the polymer backbone. Oxidation



**Figure 4** Cyclic voltammograms of (—) PC-1 and (---) Poly-PC-1 in the TBAPF<sub>6</sub>-acetonitrile, scan rate 100 mV/s, Ag-AgCl.

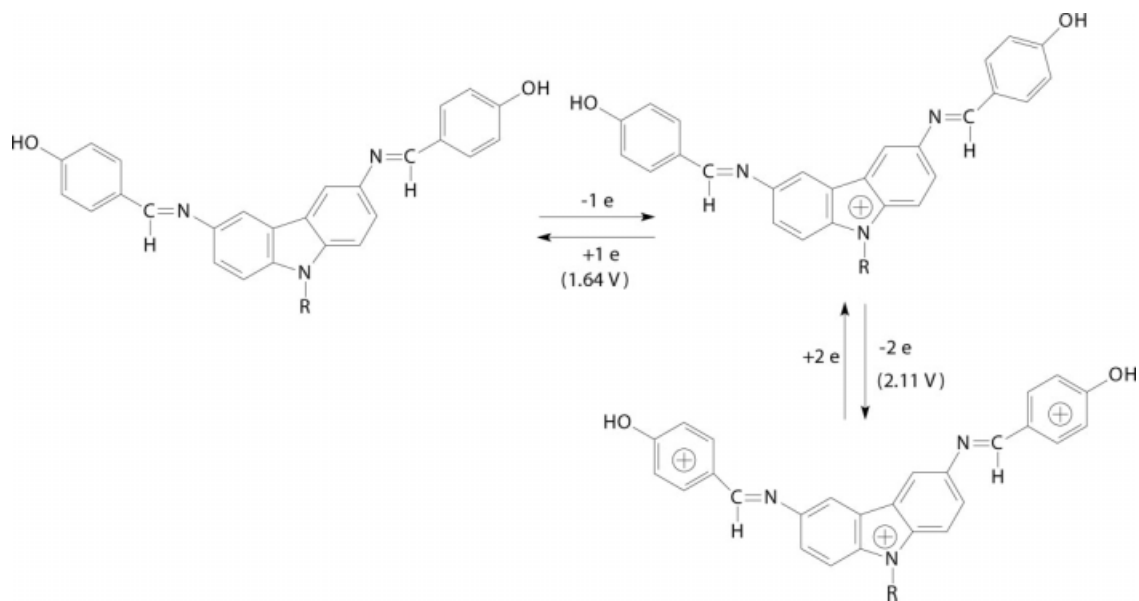
potentials of the other molecules are presented in Table III. The oxidation reaction mechanism can be proposed as shown in Scheme 3.

In general, the electrical conductivity can be taken as a function of the conjugation length of the polymer.<sup>32</sup> The conductivity also related to amount of active dopant present in the polymer as the number of charge carriers depends upon extent of the dopant concentration, providing that the other factors remain unchanged. These results show that the dopant interacts with the double bond in the polymer backbone and forms a polaronic state (radical cation) as an electron is transferred from the double bond to the dopant, creating a hole or a positive carrier at the double bond site. These holes or positive carriers are responsible for the electrical conduction in these materials. Conductivity measurements of Poly-PC compounds were carried out with an electrometer by using a four-point probe technique. Figure 5 shows the electrical conductivity results of Poly-PC compounds under iodine doping in varying periods at 25°C. First conductivities of all polymers were found to be  $\sim 10^{-11}$  S/cm and then an increase was observed after iodine doping. Although these molecules were similar to each other, conductivity measurements carried out at the end of each doping period Poly-PC-3 and Poly-PC-4 showed lower conductivities than the other polymers. The main reason may be the steric effect of alkyl substitution on carbazole units. Longer alkyl hinders the electron transfer from one polymer chain to another, reducing the electrical conductivity. So, Poly-PC-3 and Poly-PC-4,



**Scheme 2** The electrochemical reaction mechanisms of the polymers.



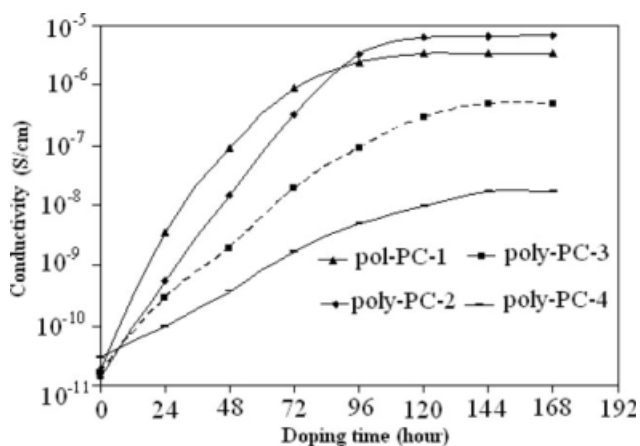


**Scheme 3** The oxidation reaction mechanisms of the polymers.

having longer alkyl chain in their structure, showed lower conductivities than Poly-PC-1 and Poly-PC-2. Also, these alkyl groups hinder the coordination of iodine with nitrogen, because of the steric effect exerted by them. Diaz et al. suggested a conductivity mechanism of imine ( $-\text{CH}=\text{N}-$ ) polymers when doped with iodine.<sup>27</sup> Furthermore, it is believed that iodine doping occurs not only on the nitrogen atoms but also on the carbazolyl rings. The conductivity mechanism over the polymer backbone is proposed as shown below (Scheme 4).

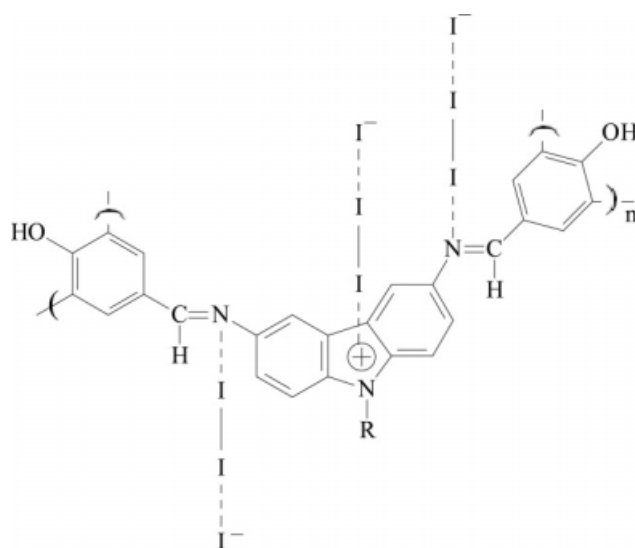
### Thermal analyses

The thermal degradations of PC and Poly-PC compounds were studied by TG-DTG-DTA analyses



**Figure 5** Change in the electrical conductivities of polymers during the process of iodine doping (done at atmospheric pressure and 25°C).

under  $\text{N}_2$  and thermal analyses results are given in Table IV and Figure 6, respectively. Because of the long conjugated band system, whole polymer products were found to be higher resistance than the monomer products as expected. For example, the initial degradation temperature of PC-1 was observed as 246°C. On the other hand, for Poly-PC-1, this value was found to be 276°C. Furthermore this polymer formed higher amounts of carbonaceous residue such as 55.80% at 1000°C. The weight losses are attributed to the alkyl groups on these molecules degrading between 260 and 350°C. It is seen that



**Scheme 4** The nitrogen atom coordination of iodine with the polymers.

TABLE IV  
Thermal Decomposition Values of All PC and Poly-PC Compounds

Compounds	TGA				% Carbine resi. at 1000°C	DTA	
	$T_{\text{on}}^{\text{a}}$	$T_{\text{max.}}^{\text{b}}$	$T_{20}^{\text{c}}$ (°C)	$T_{50}^{\text{d}}$ (°C)		$T_g$	Endo
PC-1	242	275, 490	415	–	54.12	–	238, 261
PC-2	275	473	420	–	50.51	–	–
PC-3	277	315	284	310	3.16	–	136, 325
PC-4	288	350, 472	347	473	31.18	–	–
Poly-PC-1	227	338, 510	415	–	52.53	–	–
Poly-PC-2	259	300	276	305	11.68	306	130
Poly-PC-3	270	324, 463	303	352	15.22	327	–
Poly-PC-4	265	468	398	482	33.00	310	470

<sup>a</sup> The onset temperature.

<sup>b</sup> Temperature of the maxima of the peak.

<sup>c</sup> Temperature corresponding to 20 wt % weight loss.

<sup>d</sup> Temperature corresponding to 50 wt % weight loss.  $T_g$  = glass transition temperature.

TGA curves of these compounds (Fig. 6), 1.5–8.5% wt losses were observed in the 100–175°C range. Because of C–O coupling formation, initial degradation temperature of polymers were observed to be lower than for the monomers in the TGA measurements. This result was demonstrated to be due to degradation of C–O bond at lower temperature than the C–C bond.

## CONCLUSION

The imine coupled polyphenols containing carbazole units in the main chain were synthesized by the oxidative polycondensation reaction. Molecular structures of the synthesized compounds were identified by FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectra and their results showed that all reactions were completed

successfully. According to SEC analyses, polydispersity index values of poly-PCs changed from 1.144 to 1.313. While these molecules had similar electrochemical and optical properties, they showed different electrical and thermal properties. Furthermore, at the end of the iodine doping, the conductivity of Poly-PC-1 and Poly-PC-2 were higher than that of Poly-PC-3 and Poly-PC-4. According to the TGA-DTA analyses results, Poly-PC compounds were shown to have enough resistance against thermal decomposition. Although HOMO-LUMO energy levels and electrochemical band gaps ( $E_g'$ ) of Poly-PC compounds were found to be in the range of 2.83–2.94 eV, the optical band gaps ( $E_g$ ) were measured to be 2.57 eV for all. These results may indicate that these molecules have potential for organic electronic technologies.

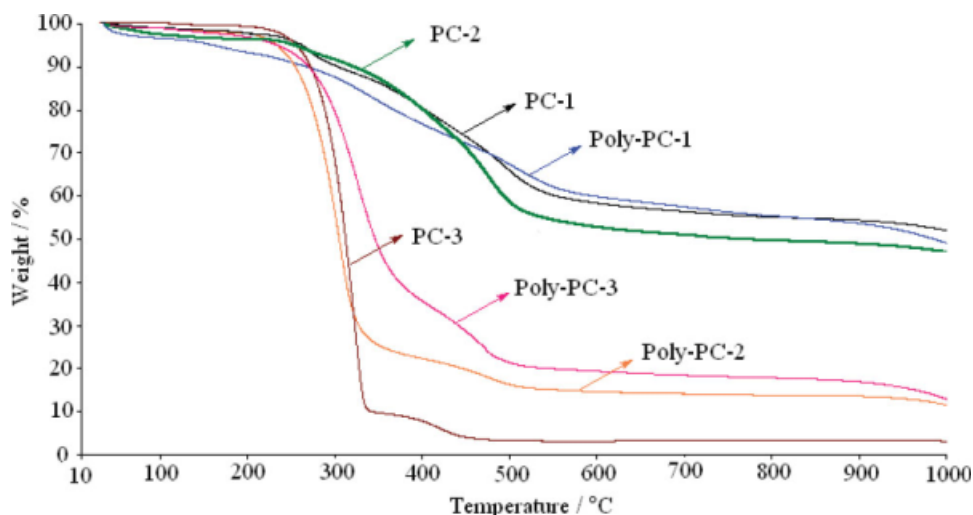


Figure 6 TGA curves of the monomers and the polymers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

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