Chemical Formation, Characterization and Properties of Polycarbazole

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ABSTRACT: Polycarbazole (PCz) was synthesized by chemical polymerization of carbazole in acetonitrile medium using ammonium persulfate as oxidant. The selection of solvent, concentration of the monomer, composition of the solvent, polymerization time, temperature, and pH were optimized to obtain better quality and yield of the polycarbazole. The synthesized polycarbazole was characterized by various techniques such as UV–Visible, FTIR, ^{1}H-NMR, ^{13}C-NMR, COSY, NOESY, and XRD spectroscopy. The solubility of the polycarbazole was tested in various solvents. The thermodynamic stability of the polycarbazole was examined by DSC and TGA-DTA analysis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 147–154, 2010

Key words: FTIR; hetero atom containing polymers; NMR; synthesis

INTRODUCTION

In recent years, electro-active and photoactive conductive polymers gained more importance because of the versatility of their applications in the fabrication of light emitting devices,[1–8] electro chromic displays,[9–11] laser dyes,[12,13] and organic transistors.[14,15] Polymer materials offer considerable processing advantages over monomer molecules since, (i) Polymer films can be generated from solution deposition techniques, (ii) They are usually glassy, and (iii) They have good mechanical and optoelectronic properties in addition to excellent corrosion resistance properties at room temperature.

The most widely studied conducting polymers are polyaniline,[16–25] polypyrrole,[26–34] and poly thiophenes.[35–40] Relatively, little attention has been paid to chemical polymerization of the above conducting polymers. Chemical polymerization is of particular importance since this synthesis is the most feasible route for the large scale production. Moreover, it was shown that chemical synthesis yields a polymer having a higher molecular weight.[41] The main drawback encountered with polymers in optoelectronic devices has been their operational stability which is largely connected with their chemical purity. Indeed, polymerization products are usually polluted by impurities that cannot be separated by distillation or sublimation. Therefore, the impurity trap charge carriers lead to a decrease in the device efficiency and shortening of lifetime.

Furthermore, among the three basic colors required for the multi color displays, many efforts have been devoted to obtain blue light emitting polymeric materials since the blue luminescence is difficult to achieve with inorganic materials. Various approaches have been used to obtain such polymers such as use of oligomers with high-energy gap and that of copolymers with short conjugated segment. Oligomers usually exhibit a poor film forming ability and high tendency for crystallization. Another strategy has been adopted by synthesizing polymers consists of short conjugated segments interconnected by solublizing nonconjugated species. Such materials are expected to retain the electronic properties of conjugated oligomer blocks and to possess the processability and long-term morphological stability of the higher molecular weight polymers.

Recently, various π-conjugated poly(arylene)s containing electron withdrawing imine nitrogen(s) in the arylene units have been prepared and they have been converted into electrically conducting materials by reduction (*n*-doping).[42] However, most of the studies on the poly(arylenes)s with imine nitrogen(s) have been carried out with these compounds constituted of six-membered and five-membered rings (e.g., polypyridine, polythiazole) and only a few studies have been reported on π-conjugated *N*-vinylcarbazole and 1,4,5,8,9-pentamethyl carbazole (Fig. 1) containing the electron withdrawing imine nitrogen(s).

Although preparation of poly(3,6-carbazole) with FeCl$_3$ has been attempted,[43] only optical property of

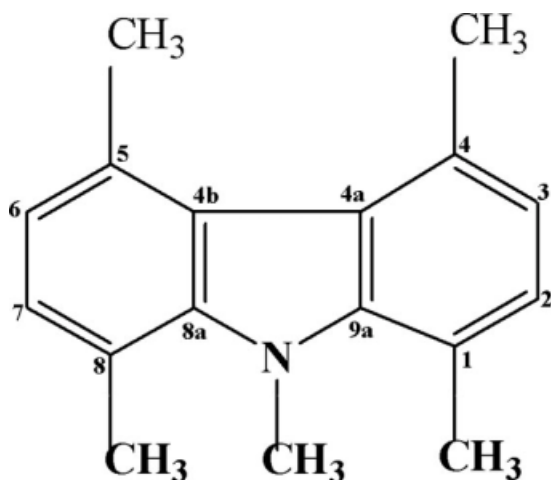*Correspondence to:* V. Raj (alaguraj2@rediffmail.com).

Figure 1 Structure of penta methyl carbazole.

the product has been studied and detailed characterization of the product has not been reported. In addition to the above said polymers, some other electro-active polymers were also synthesized and reported for optoelectronic devices. Siove and Ades[43] studied the chemical oxidation of *N*-alkyl carbazoles by $FeCl_3$ which exclusively and quantitatively yielded the dimer (bicarbazyl). They have also reported the single-layer organic light emitting diodes based on the *N-N* diethyl-3, 3′-bicarbazyl with indium tin oxide and Mg electrode. However, these OLEDs showed a low stability that has been attributed to morphological changes of the carbazolic emission layer. Indeed, these films based on bicarbazyl species tend to show dendrities on defect locations after a few days in air, which affects both the homogeneity of the film and performance of the device. As these dendrites grow up, blue light emission decreases and finally leads to the breakdown of the diodes. To overcome this drawback, Benazzi et al.[44] investigated the possibility of the incorporating bicarbazyl dimeric moieties along macromolecular chains while keeping their electro-active properties. Cloutex et al.[45] reported the synthesis, characterization, purification, physicochemical, and photoluminescence properties of poly(3, 3′-bicarbazyl *N*, *N*-octylene).

Maruyama et al.[46] reported the preparation and electrically conducting properties of π-conjugated polythiazole. Blue light emission requires wide band gap materials. Polyfluorene,[47,48] 3,6-carbazole based homopolymers,[45,49] and their copolymers[50–54] have been developed because of their interesting blue luminescence due to their limited π-conjugation. Recently, poly(2,7 carbazole) has been synthesized and was found to exhibit a limited solubility and blue luminescence due to the biphenilic type conjugation along the backbone.[55–57] However, electroluminescence performances and blue color purity

obtained with polycarbazole family are far from those obtained with small carbazole molecules. Romero et al.[58] reported the synthesis and luminescence properties of *N*-ethyl carbazole dimers. Because of the limiting solubility in common organic solvents, their infusibility and photoluminescence properties of the above synthesized polymers, there is a constant search for a new class of polymers which fulfills all the requirements of optoelectronic devices.

In this work, we report the synthesis, characterization, and properties of a new conducting polymer, polycarbazole by chemical oxidative polymerization.

EXPERIMENTAL

Materials

Carbazole (Kemphasol) was recrystallized from hexane and obtained as light brownish needles. Acetonitrile (Merck) was freshly distilled before utilization. Ammonium persulfate (Rankem) was used as such. All other solvents were of AR quality and used after necessary purification.

Monomer, i.e., carbazole ^{1}H-NMR ($CDCl_3$, 200 MHz, δ ppm): 7.1 ($2H$, $H_{3,6}$), 7.3 ($2H$, $H_{1,8}$), 7.4 ($2H$, $H_{2,7}$), 8.0 N—H proton of the pyrrrole nuclei (Fig. 2).^{13}C-NMR ($CDCl_3$, 50 MHz, δ ppm): 139 (C_{9a}), 130 (C_2), 125 ($C_{3,6}$), 123 ($C_{4a,4b}$), 121 (C_5), 120 ($C_{4,7}$), 110 (C_{18}) which is shown in Figure 3.

Synthesis of polymer

In a typical polymerization system, $1 \times 10^{-4} M$ of carbazole was dissolved in 15 cc^3 of CH_3CN moderately and magnetically stirred. Ammonium persulfate ($1 \times 10^{-3} M$) was dissolved in 8 cc^3 of 95% CH_3 CN and then the solute was added in drops to the carbazole solution. The system was kept under stirring at room temperature for 3 h and thereafter, the solution was poured in an excess of methanol. The green precipitate was washed several times with distilled water, successively filtered, and then dried. This material was dried in a vacuum oven and redissolved in dry chloroform. The small insoluble par (gel) was then isolated by filtration and the soluble fraction was poured into methanol to give off white precipitate. This reaction was shown in Figure 4

From Figure 5, ^{1}H-NMR ($CDCl_3$, 200 MHz, δ ppm): three singlets are obtained. 7.5 ($2H_{2,7}$), 7.25 ($2H_{1,8}$), N—H proton of the pyrrole nuclei. 8.5 ($C_{3,6}$, aromatic proton of the terminal ring). ^{13}C-NMR ($CDCl_3$, 50 MHz, δ ppm); 140 ($C_{8a,9a}$), 123 ($C_{4a,4b}$). 121 (C_5), 120 ($C_{4,7}$), 110 (C_{18}) which is shown in Figure 6
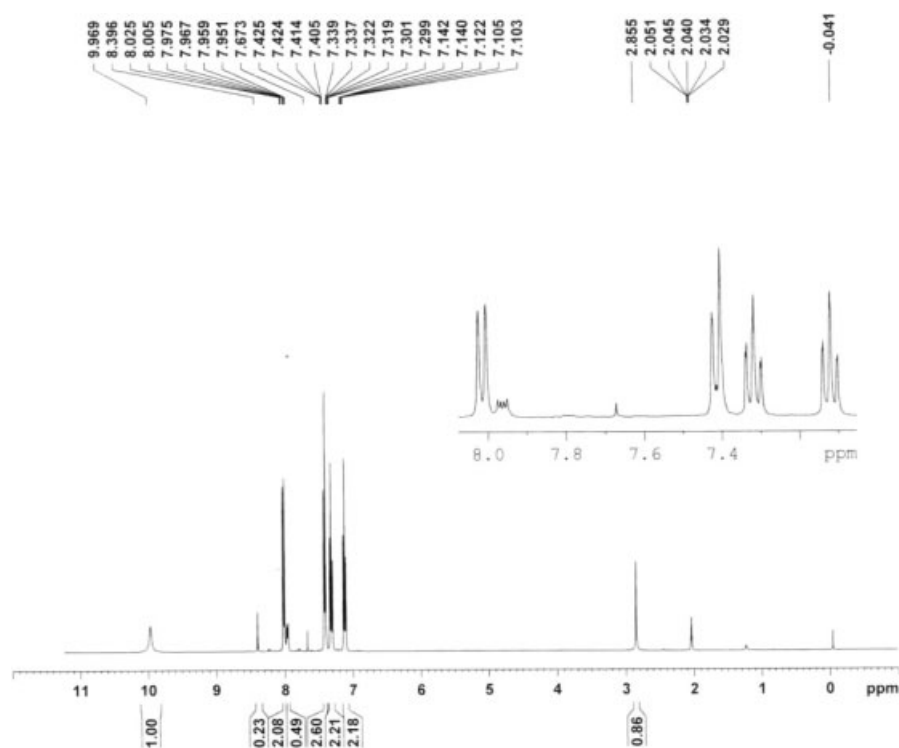
Figure 2 ¹H-NMR spectrum of carbazole.

Characterization

Solubility of the synthesized PCz was tested with various solvents such as ethanol, methanol, dioxan, ether, n-hexane, chloroform, toluene, and DMF. UV–visible spectroscopy was carried out in a Perkin–Elmer UV–Visible Spectrometer using 0.5 cm path quartz cells in the range 190–1100 nm. Dry polycarbazole powder was compressed into pellets, 13 mm in diameter and 1 mm thick, and the conductance
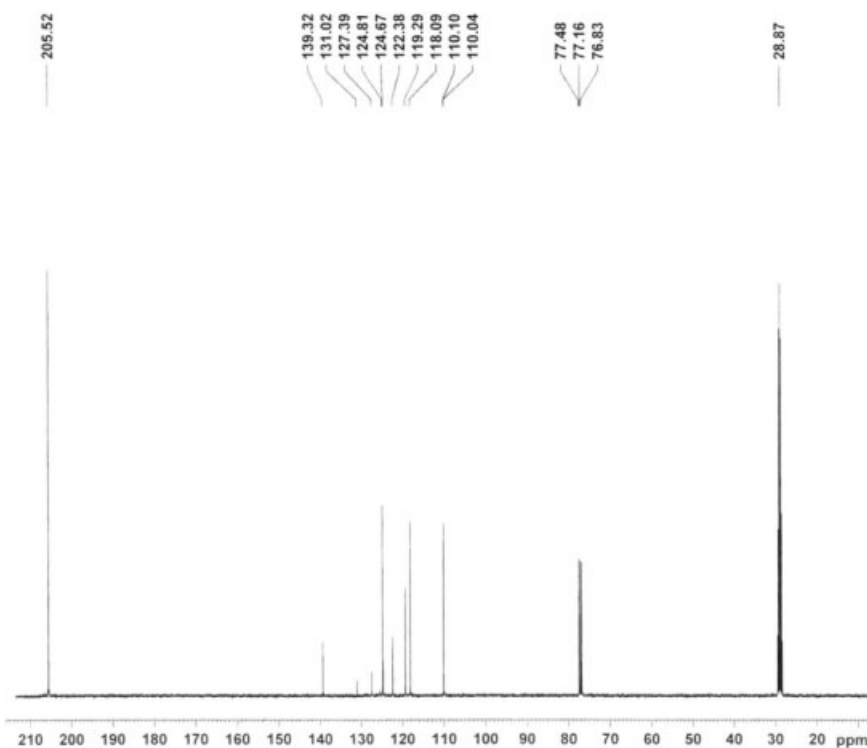

Figure 3 ¹³C-NMR spectrum of carbazole.

$(NH_4 S_2 O_8)$

$$CZ \xrightarrow{} CZ \sim\sim\sim\sim CZ (\sim\sim\sim\sim CZ)_n \sim\sim\sim$$
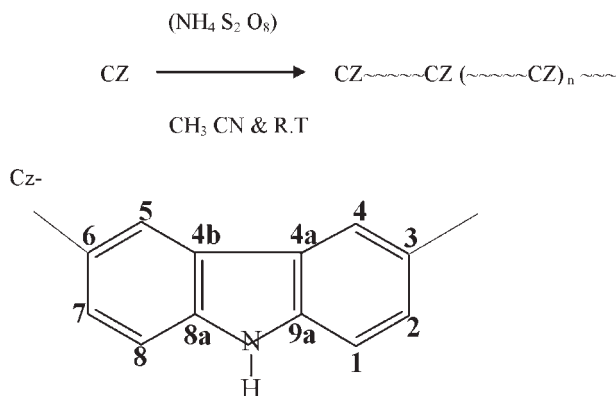
$CH_3 CN$ & R.T

Figure 4 Schematic diagram of formation of polycarbazole from its monomer.

was measured by four-probe method at various temperatures ranging from 308 to 368 K.

NMR (^{1}H, ^{13}C, COSY, and NOESY) spectra were recorded in CDCl$_3$ solution with a Brucker AC 200 spectrometer, at 200 and 50 MHz. All the chemical shifts (∂ in ppm) were referenced to tetramethyl silane (TMS). FTIR spectrum of the polymer was recorded on Perkin-Elmer FTIR spectrometer with KBr pressed pellet.

Thermal stability of the polymer was determined using Mettler TA 3000 Analyzer and TGA-DSC 910S Differential scanning calorimeter. The thermogram was recorded with 5–10 mg of sample at a heating rate of 293 K min^{-1} in nitrogen atmosphere. XRD was performed on a Phillips X-ray diffractometer
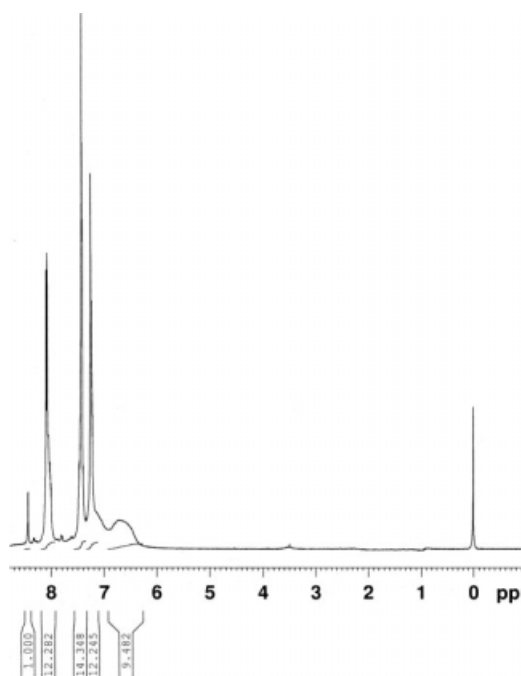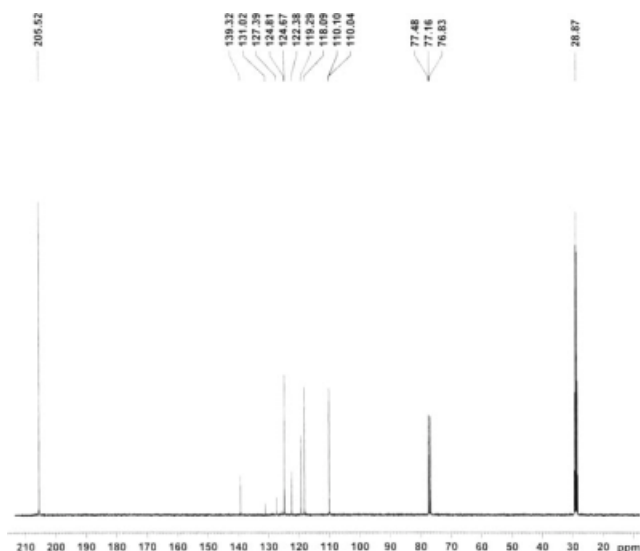

Figure 6 ^{13}C-NMR spectrum of polycarbazole.

using Cu k∞ radiation source operating at 50 kV and 30 mA.

RESULTS AND DISCUSSION

Solubility of polycarbazole

Polycarbazole was found to be insoluble in almost all inorganic solvents and most of the organic solvents. It is completely soluble in CHCl$_3$, CDCl$_3$, CH$_3$CN, THF, DMSO, and DMF.

UV–visible spectral study

In Figure 7, UV–Visible spectrum of polycarbazole displays strong absorption peaks at 302 and 317 nm and bands of lower intensities at longer wavelength around 247 and 372 nm. All these absorption bands are characteristics of the polymer.[59] They are themselves red-shifted.
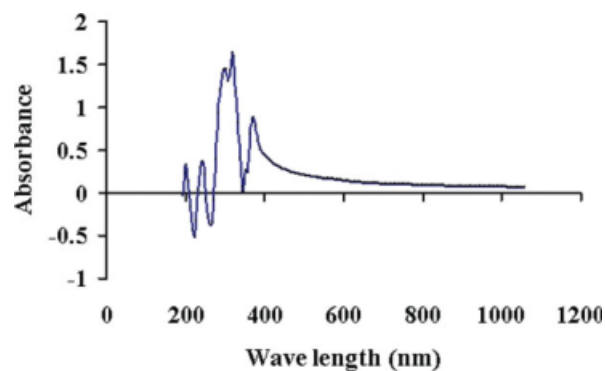

Figure 5 ^{1}H-NMR spectrum of polycarbazole.

Figure 7 UV–Visible spectrum of polycarbazole in CHCl$_3$ solution (quartz cell) of concentration $5 \times 10^{-4} M$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
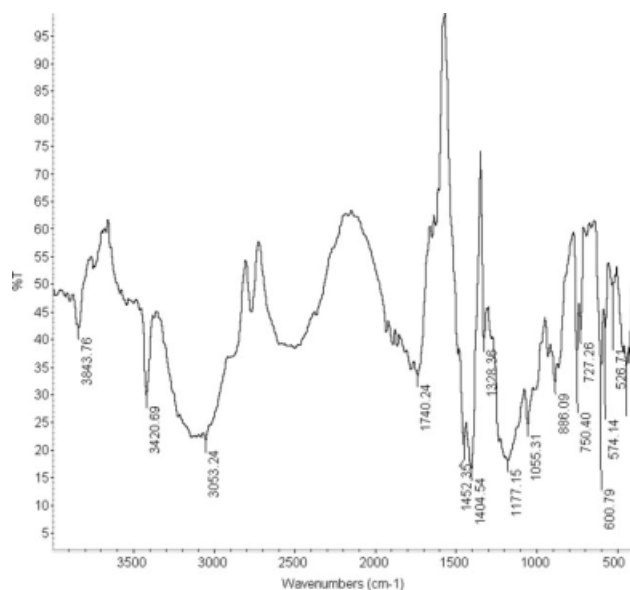
Figure 8 Fourier transform infrared (FTIR) spectral pattern of polycarbazole.

FTIR characteristics

The FTIR spectra of polycarbazole are given in Figure 8 and the various bands assigned are summarized in the Table I.

Polycarbazole seems to be essentially composed of the recurring carbazole 2, 5-diyl unit. However, the polymer also seems to be more susceptible to chemical reaction due to the presence of chemically active hydrogen at the 4th position and its IR absorption bands are broadened.[60]

^{1}H-NMR spectral characteristics

The ^{1}H-NMR spectrum of Cz (monomer) and PCz were used to examine the chemical structure of the polymer and it is shown in the Figure 5. The five-membered heteroaromatic protons (1,8) are at 7.25 ppm. The benzenic proton of the aromatic ring is at 7.5 ppm (2,7). The signal at 8.1 ppm is due to N—H proton of the pyrrole nuclei. The aromatic proton of the terminal ring was observed at 8.5 ppm (3,6).

^{1}H-NMR analysis of polycarbazole disclosed that the oxidative coupling essentially occurred as anticipated in 3 and 6th position of the carbazole moieties and are consistent with the expected structure. As polymerization precedes, 3, 6 proton peaks of the monomer at 7.1 ppm as well as the corresponding tertiary carbon at125 ppm disappear and a new signal ascribed to the quaternary carbon of the 3, 6 polymer linkage appears at 130.68 ppm. No abnormal linkages resulting from 2, 7 coupling were detected in the ^{1}H-NMR spectra of PCz[43] which is shown in Figure 9.

Figure 10 shows the COSY ^{1}H-NMR spectrum of polycarbozole. Both axes relate to proton chemical shift and the peaks appeared on the diagonal at frequencies (the same frequencies at each axis) corresponding to the resonances in the normal ^{1}H-NMR spectrum. The appearance of off-diagonal peaks implies that there are coupling between protons of 2 and 7 with 1 and 8 (d, 7.5 ppm) and protons of 1 and 8 with protons 2 and 7 and N—H (t, 7.25 ppm) and N—H protons of pyrrole nuclei with protons of 1 and 8 (d, 8.1 ppm).

Figure 11 shows the NOESY ^{1}H-NMR spectrum of polycarbozole. Similar off-diagonal peaks corresponding to the above said protons with their couplings are observed in the same resonance positions as that of normal ^{1}H-NMR spectrum and COSY spectrum.

Thermal stability

The thermal stability of polycarbazole sample was studied by TGA. Figure 12 presents the curves of weight loss versus temperature. The first significant weight loss occurs at temperature between 335 and 373 K. It is known that PCz is hygroscopic and during the heating to 373 K the residual water evaporates[61] then the main loss which corresponds to loss of dopant bound to the polymer chain starts at about 466–505 K with weight loss of 64%. The second stage of degradation starts at 573–673 K with weight loss of 20%. This may be due to the successive cleaving of the backbone of the polymer.[62] In DSC

TABLE I
FTIR Spectral Pattern Characteristics of Polycarbazole

| System	Peaks (cm^{-1})	Assignments
PCz	600	C=C out of plane bending vibration of the aromatic ring
	727	Ring deformation of substituted aromatic structure
	750	>CH$_2$ Rocking vibration due to tail to tail addition
	1328	C—H out of plane bending vibration of the aromatic ring
	1404 and 1452	Ring stretching vibration of carbazole moiety
	3053	N—H stretching absorption of heteroaromatics
	3420	γ—OH bands of water nitrogen containing heterocycles
	1740	δ—OH often form water adducts [43]
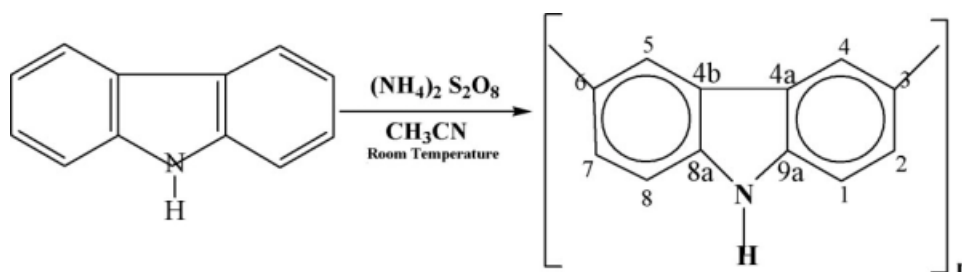
Figure 9 Schematic diagram of polymerization of carbazole.

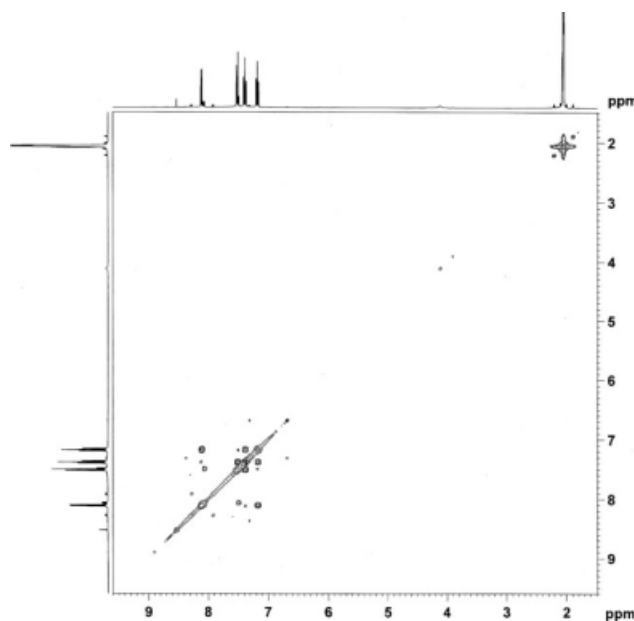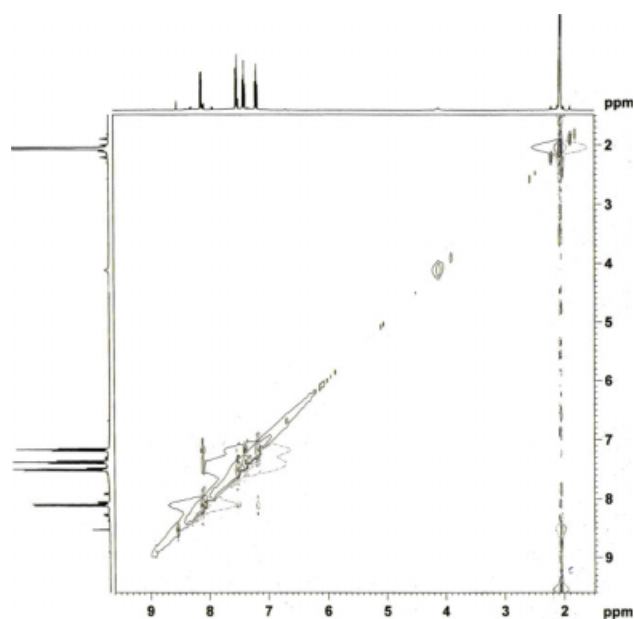**Figure 10** COSY ^{1}H-NMR spectrum of polycarbazole.

Figure 11 NOESY ^{1}H-NMR spectrum of polycarbazole. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

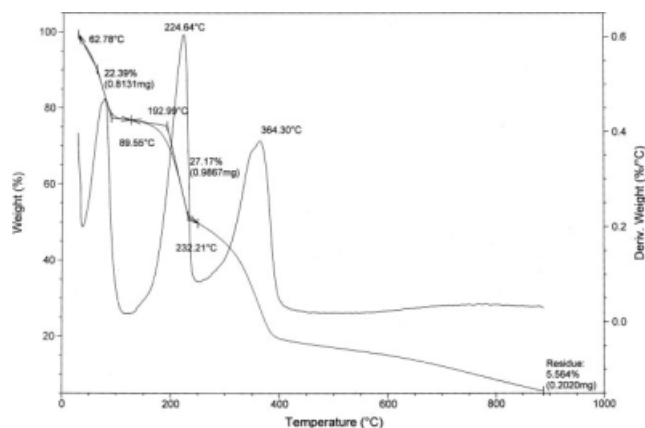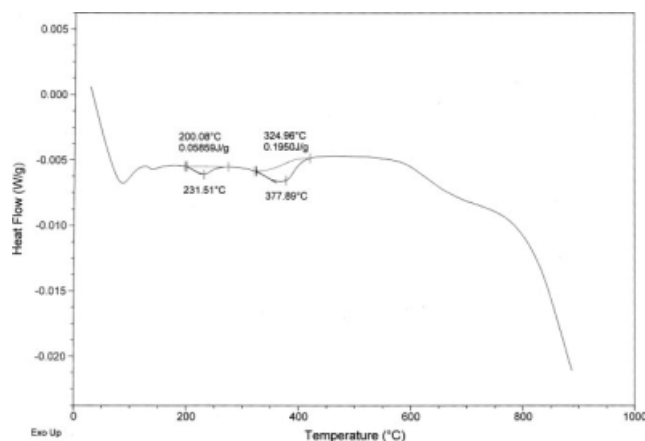**Figure 12** TGA/DTA curves of polycarbazole.

Figure 13 Differential scanning calorimetric analysis of polycarbazole.

(Differential Scanning Calorimetry), the exothermic transitions are rarely seen, whereas the endothermic transitions are seen in all polymers. The endothermic peaks are present between 335 and 423 K arising due to the removal of water molecules present in polymer and other endothermic peaks between 474 and 601 K arising due to the removal of dopant ions.[63] From Figure 13, the exothermic peak also found between 504 and 590 K, which is assigned to the interchain crosslinking in the polymer.[64]
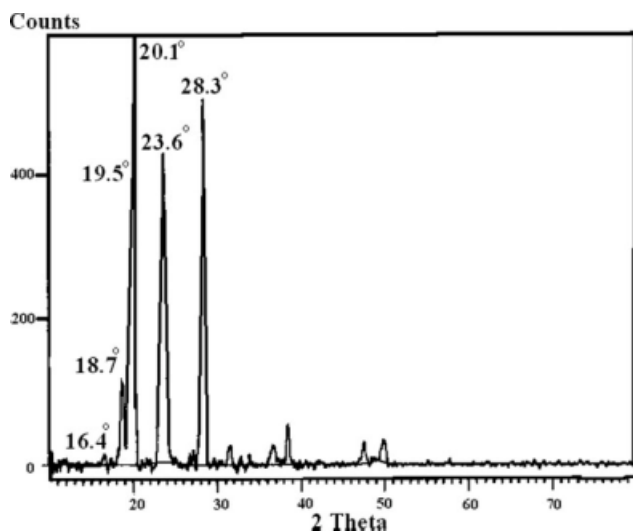
Figure 14 Powder X-ray diffraction pattern of polycarbazole.

X-ray diffraction measurements

The XRD pattern of the PCz is shown in Figure 12. There are three main peaks at about $2\theta = 20.1°$, 23.6°, 29.4°, and three small peaks 38.3°, 47.4°, and 50.04°. The XRD pattern exhibit a sharp diffraction peaks at 19.5° (58.97%), 20.1° (100%), 23.6° (78.56%), and 28.3° (88.40%). The peak centered at $2\theta = 20.1°$ may ascribed to the periodicity parallel to the polymer chain, whereas the weak peaks at high angles may be caused by periodicity perpendicular to the polymer chain[65] (Fig. 14).

Conductivity

The electrical conductivity of the polymer was measured on pellets at room temperature by using the four-probe method of Vander Pauw[66] pressed at 2 T cm^{-2} is close to 10^{-5} S cm^{-1} when doped with ammonium persulfate. It is evident that conductivity increases steadily up to 65°C showing semiconductor behavior, afterward, it decreases. A similar trend has been reported for poly(N-ethyl aniline).[67] The decrease in conductivity after the well-noticeable transition temperature is attributed to the loss of

TABLE II
Electrical Conductivity of Polycarbazole at Various Temperatures

Temperature (°C)	Conductivity (S cm^{-1}) × 10^{-5}
35	2.68
45	3.4
55	5.7
65	8.2
95	0.1

water molecules.[67] TGA results also support this. The conductivity of the polymer is given in Table II.

CONCLUSIONS

Polycarbazole was synthesized by chemical polymerization method using ammonium persulfate as oxidant. The conditions for the synthesis of polycarbazole with good yield were optimized. The synthesized polymer was characterized and confirmed by by UV-Visible, FT-IR, ^{1}H-NMR and XRD spectroscopic techniques. Solubility, conductivity and thermal stability of the synthesized polycarbazole were also determined by appropriate methods.

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