

Electrochemical Synthesis and Characterization of Polycarbazole

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ABSTRACT: Electroinitiated polymerization of carbazole was achieved in acetonitrile by direct electron transfer via constant potential electrolysis based on anodic peak potentials. The anodic peak potential of carbazole was determined by cyclic voltammetry to be + 1.4V. It has been observed that polymer yield increased with some factors, such as time, monomer concentration, and polymerization potential. Conducting polycarbazole material obtained on a platinum anode electrode was characterized by FT-IR, TGA, and con-

ductance measurements. The conductivities of samples were measured to be about 10^{-3} – 10^{-4} S/cm by the four-probe method. Temperature-dependence of electrical resistance values of polycarbazole between 30°–125°C suggest that it can be used as a thermal sensor. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 894–898, 2005

Key words: polycarbazole; conducting polymers; electroinitiated polymerization

INTRODUCTION

There are extensive studies in the literature concerning the synthesis, characterization, and application of conductive polymers, such as polypyrrole, polyaniline, polythiophene, and poly(*N*-vinyl carbazole),^{1–4} due to their technical utility. Polycarbazole is one of a group of relatively new conducting polymers with good electrochemical characteristics, and its conductive form can easily be obtained by the electrochemical method.⁵

Anodic oxidation of carbazole and its *N*-substituted derivatives were studied by Ambrose et al.⁶ They investigated the reactivity of cation radicals formed from 76 ring substituted carbazole using electrochemical and spectroscopic techniques. It was reported that the 3, 6, and 9 positions on carbazole were extremely reactive and anodic oxidation of carbazole produced very unstable cations, such as 9,9'- and 3,3'-bicarbazyls.

Pasquali et al.³ reported that the electropolymerization in a 75% CH₃OH and 25% HClO₄ mixture on Pt electrode conductivity of thin polycarbazole films peeled off from the working electrode was found to be around 10^{-4} S/cm.

Anodic oxidation of carbazole in aqueous alcoholic HClO₄ has been reported by Mengoli et al.⁷ In another study, polycarbazole has been post doped with iodine and characterized by electrical conductivity measure-

ments, x-ray photoelectron spectroscopy, and electron spin rezonans.⁸

Polycarbazole is one of the conducting polymers that can be used in various applications. The copper(II) ion selective microelectrochemical transistor was developed using polycarbazole.⁹ The selectivity of the device for some metal ions, such as Cu(II), Cu(I), Fe(II), Fe(III), and Zn(II), was also reported.⁹ Polycarbazole has a potential as the cathode active material for secondary batteries.¹⁰

EXPERIMENTAL

Materials

Carbazole (Aldrich) and acetonitrile (Merck) were used as supplied. The supporting electrolyte, tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich), was used after being dried under vacuum.

Procedures

The cyclic voltammograms were obtained via a three-electrode cell with a 1-mm long Pt wire working, a 2-cm coiled Pt wire counter electrode, and an Ag wire reference electrode using a Wenking POS-88 potentiostat (Germany) and a Linseis LY (6100-II) X-Y recorder (Germany). The cyclic voltammetric measurements were carried out in acetonitrile-TBAFB under nitrogen atmosphere at room temperature.

The electrochemical polymerization of carbazole was performed in an H-cell, the details of which have been discussed previously.¹¹ The working and counter

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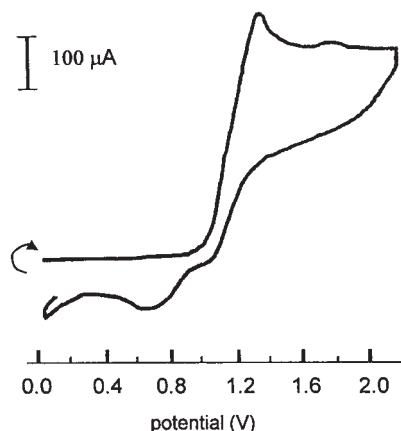


Figure 1 Cyclic voltammogram of carbazole in acetonitrile-TBAFB at a scan rate of 50 mV/s.

electrodes were Pt foils with an area of 1.8 cm², and the reference electrode was Ag wire.

Characterization

A Jasco FT-IR-300E model spectrophotometer was used for the FT-IR spectra of the sample dispersed in a KBr disc.

The thermogravimetric analysis was carried out in a nitrogen atmosphere with a flow rate of 200 mL/min using a General V4.10 DuPont 2000 Model thermal analyzer. The samples were heated to 1100°C at a rate of 10°C/min starting from room temperature.

A four-probe head equipped with a Keithley programmable current source, which is sensitive to the nA (nanoampere) level, was used to measure conductivities of pressed disc samples.

The temperature dependence of the pressed disc samples was measured over a temperature range of 30 to 125°C. The polymeric sample was placed in a temperature-controlled chamber, and the resistance of the sample was recorded varying the temperature.

RESULTS AND DISCUSSION

Figure 1 indicates cyclic voltammogram (CV) of carbazole recorded in acetonitrile/TBAFB. As seen from CV, carbazole has two oxidation potentials, one at + 1.4 V discretely and the other at + 1.7 V in a shoulder shape.

CV results obtained at first, second, and fifth cycles are given Figure 2. A new peak appeared at + 0.9 V, and the shoulder at + 1.7 V disappeared after the first cycle. The new peak at + 0.9 V is due to the oxidation of polycarbazole.⁷

Returning from the first oxidation peak at + 1.4 V, the peak of + 0.9 V did not disappear (Fig. 3). These data indicate that carbazole can be oxidatively poly-

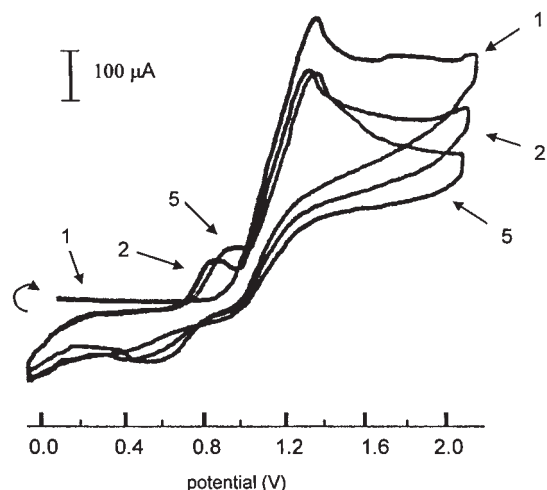


Figure 2 Multisweep cyclic voltammogram of carbazole in acetonitrile-TBAFB at a scan rate of 50 mV/s.

merized upon radical cation at + 1.4 V, giving polycarbazole. After the first cycle, the peak intensity at + 0.9 V increases, and potentials shift toward higher values (Fig. 2).

The structure of polycarbazole has been investigated by means of FT-IR spectra. Figures 4a and b show FT-IR spectra of carbazole and conductive polycarbazole, respectively. FT-IR spectra of polymer samples obtained at different experimental conditions are similar to that of Figure 4b. The peaks at 724 cm⁻¹ and 748 cm⁻¹ observed at the FT-IR spectrum of carbazole do not appear in the FT-IR spectrum of polycarbazole. These two peaks are due to the unsubstituted carbazole.⁶ This observation indicates that polymerization may proceed from the 3 and 6 positions. On the other hand, the peaks observed at 800 cm⁻¹ and 875 cm⁻¹ in

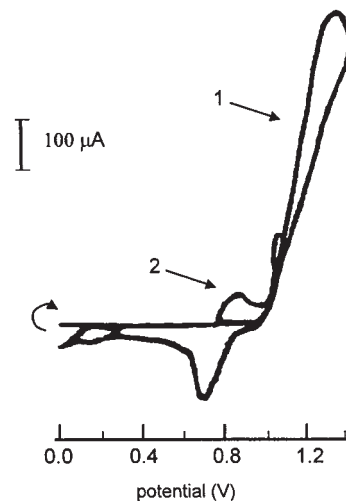


Figure 3 Multisweep cyclic voltammogram of polycarbazole in acetonitrile-TBAFB at a scan rate of 50 mV/s.

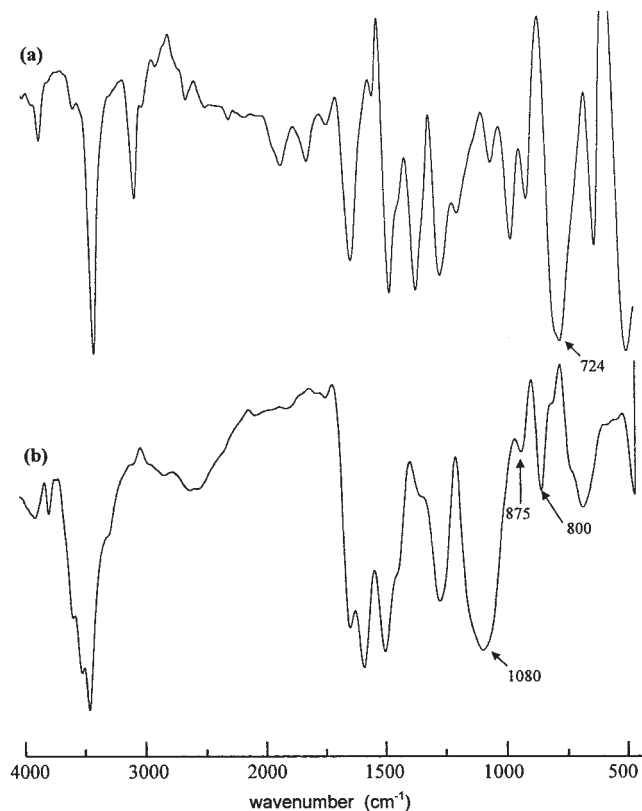


Figure 4 FT-IR absorption spectrum of (a) carbazole and (b) polycarbazole in KBr.

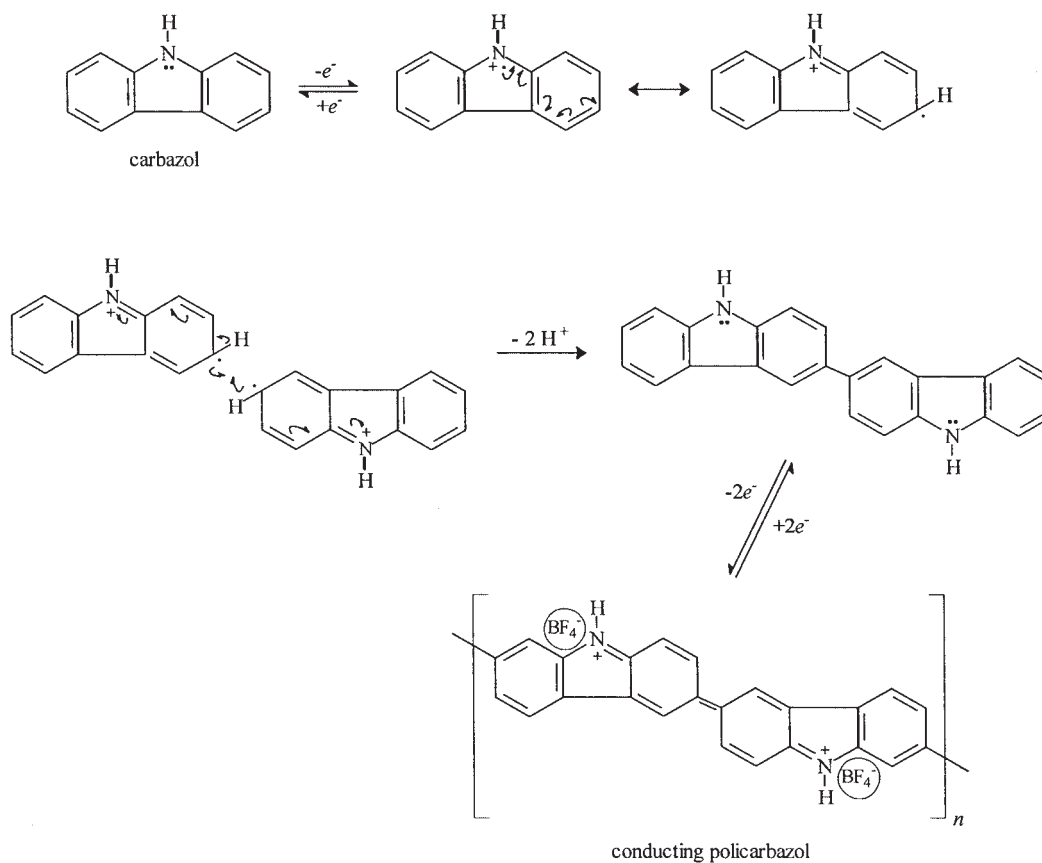


Figure 5 Proposed mechanistic scheme for the electropolymerization of carbazole.

the spectrum of polycarbazole are due to the trisubstituted benzene ring^{12,13} (Fig. 4b). These peaks indicate the existence of para-substitution.⁶

The characteristic 1080 cm^{-1} band, which is due to the BF_4^- anion¹⁴ coming from the electrolyte, was observed at the FT-IR spectrum of polycarbazole. This band does not exist at the FT-IR spectrum of carbazole.

The electrochemical polymerization mechanism of carbazole proceeded as given in Figure 5. According to this mechanism, carbazole is first oxidized at the anode, giving 3,3'-dicarbazyl cation,⁶ and polymerization proceeds in successive steps as given in Figure 5.

The conductivities of polycarbazole samples obtained were around 10^{-3} S/cm . Samples were kept at atmospheric conditions, and then conductivities were followed for 150 days. The results are given in Figure 6. During the first 20 days, conductivity values decreased gradually. For the following days, the decreasing rate in conductivity becomes slower. At the end of 130 days, polymer conductivity drops to half of its original value.

When potential is applied, the surface of the working electrode is coated with dark green film, and the solution is converted into a green color, which is indicative of dimer, trimer, etc.

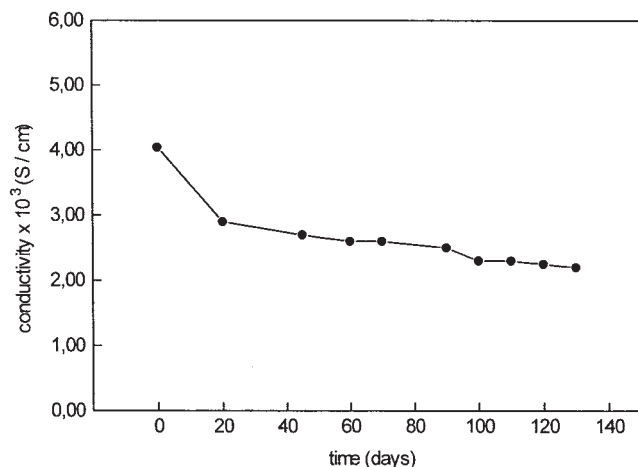


Figure 6 Effect of time on conductivity of polycarbazole.

Figure 7 displays the effect of temperature on polymer yield. As seen from Figure 7, polymer yield increases with increasing temperature and then almost remains constant after 35°C.

Polymer yield-potential relations are given in Figure 8. As seen from Figure 8, polymer yield increases with the increasing potential. At potentials of + 1.4 V and + 2.1 V, polymer yields are 15 and 45%, respectively. Current, or in other terms radical cation concentration, increases depending on the potentials employed. At higher potentials ($E_{pa} > + 1.4$ V), some other active species may be formed in the anode compartment by a second electron transfer.

The effect of monomer concentration and time on polymer yield were examined at 0.02, 0.005, and 0.0025M carbazol concentrations (Fig. 9). Polymer yield increases with time in 15 h-electrolysis and does not change significantly even if the electrolysis period is made longer. An increase at monomer concentration causes the formation of a higher amount of radical

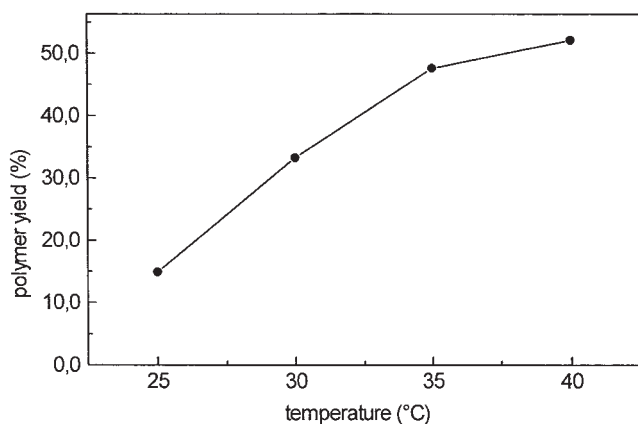


Figure 7 Effect of temperature on rate of polymerization of carbazole.

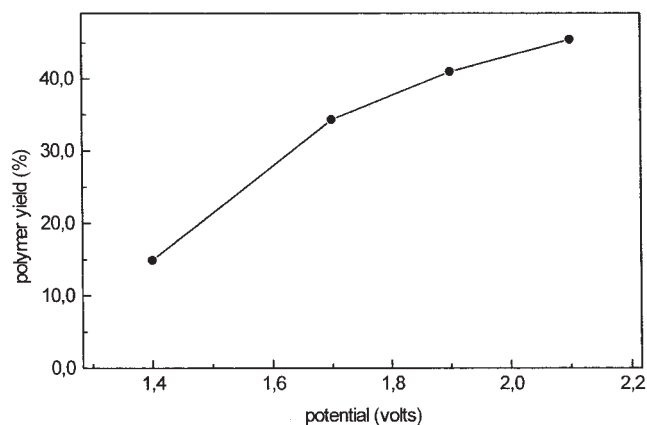


Figure 8 Effect of polymerization potential on rate of polymerization of carbazole.

cation and indirectly causes an increase at the polymerization rate.

Figure 10 shows a thermogram of conductive polycarbazole obtained at + 1.4 V electrolysis at 25°C. Here, weight loss was followed at different temperatures and total weight loss reaches 50% of its original polymer quantity at 1100°C.

Figure 11 reveals the change in resistance with temperatures for a polycarbazole sample. The pelleted sample was heated from 30 to 125°C gradually, and resistance was recorded at certain intervals. The same sample was cooled from 125 to 30°C gradually, and resistance measurements were done as before. This heating-cooling process was repeated 4 times. As the temperature increases, the polymer resistance decreases and *vice versa*. As a result, conductivity increases with decreasing temperature. The approximate resistance for this sample was 4.00 k Ω at 30°C. It dropped to 1 k Ω at 125°C. At the successive steps,

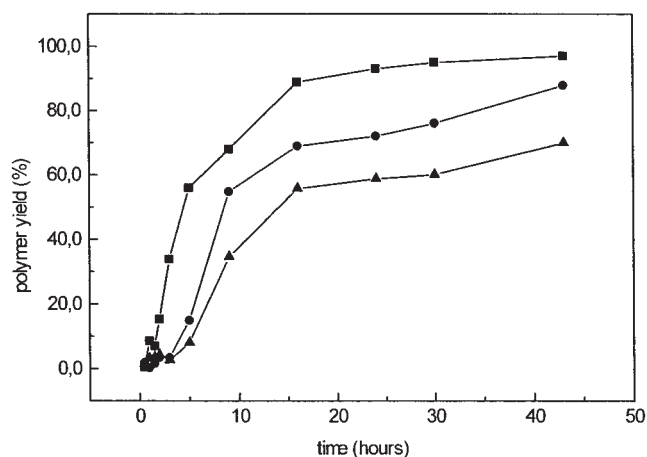


Figure 9 Effect of carbazole concentration and time on rate of polymerization of carbazole: (■) 0.0200M, (●) 0.0050M, and (▲) 0.025M.

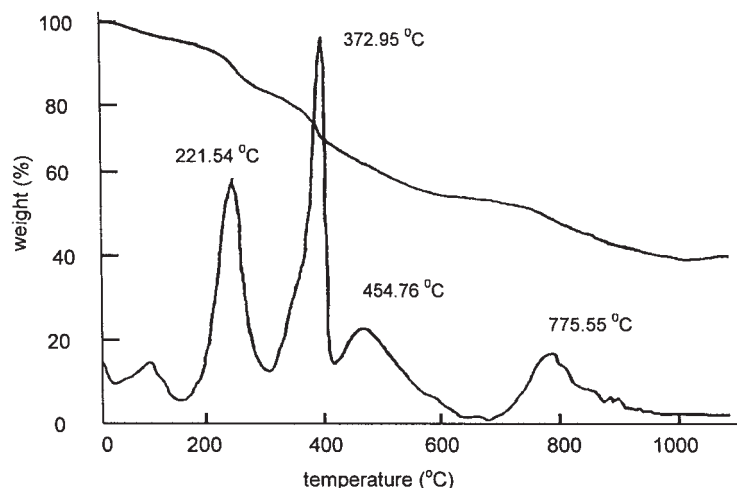


Figure 10 Thermogram of polycarbazole obtained at +1.4 V electrolysis.

repeated cycles indicated that the resistance values at 30°C and 125°C were constant as 7 kΩ and 1 kΩ, respectively. This reproducibility of resistance values indicates that polycarbazole can be used as a temperature-sensitive material.

CONCLUSIONS

Carbazol can be polymerized using acetonitrile/TBAFB as a solvent-electrolyte couple by the electrochemical way. Polymer yield increased with increasing monomer concentration, temperature, and potential. The maximum polymer yield was obtained at 15 hours of electrolysis. Conductivities of polycarbazole samples obtained at different conditions have been

measured to be about 10^{-3} – 10^{-4} S/cm. Since the polycarbazole sample has reproducible resistance values between 30 and 125°C, the polycarbazole sample can be used as a thermal sensor.

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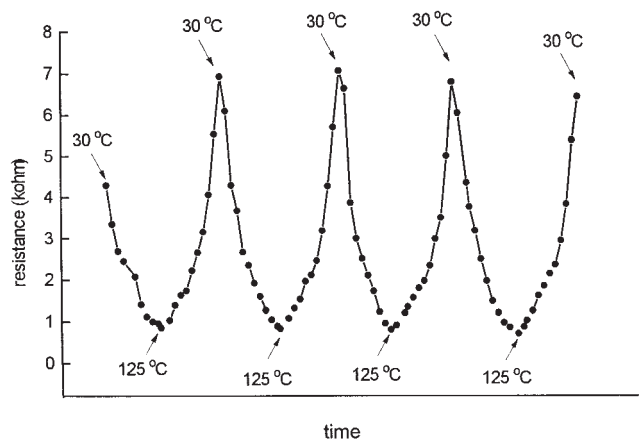


Figure 11 Relationship between the changes in resistance and temperatures for polycarbazole.