



Electrolyte effects on various properties of polycarbazole

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ABSTRACT

Effect of electrolyte during electrochemical synthesis of polycarbazole (PCz) is reported in this paper. Two different supporting electrolytes tetrabutylammonium perchlorate (TBAClO₄) and tetrabutylammonium tetrafluoroborate (TBABF₄) dissolved in acetonitrile are used for the synthesis of PCz. The electrolyte effect with regard to yield, structure, electroactivity, crystallinity and thermal stability of the polymer is studied through various techniques including XRD, cyclic voltammetry, differential scanning calorimetry and electrochemical impedance spectroscopy. High doping and facilitation of dopant ion movement in the case of PCz/TBAClO₄ in comparison to PCz/TBABF₄ film is revealed in conductivity measurements and electrochemical investigations. XRD shows a significant difference in the crystallinity of the polymers synthesized using in two different electrolytes. Melting point of the conducting polymer is also observed for the first time during thermal investigations (in case of PCz/TBABF₄). The amorphous to crystalline transformation of PCz is also observed on heating. A comparative analysis of both the electrolytes also shows that TBAClO₄ is a better supporting electrolyte than TBABF₄ in various aspects for synthesis of PCz.

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1. Introduction

Conducting polymers such as polypyrrole, polyaniline, polythiophene, and poly (N-vinyl carbazole) have been extensively studied for their synthesis, characterization and applications [1–7]. However, lately other classes of polymers like polycarbazole are gaining considerable attention due potential applications in light emitting diodes (OLED); as green and blue light emission was achieved by using carbazole (Cz) derivatives [8–15], sensors [16] and rechargeable batteries [17]. Anodic oxidation of carbazole and its N-substituted derivatives were extensively studied by Ambrose et al. [18]. They investigated the reactivity of cation radicals formed from 76 ring substituted carbazole using electrochemical and spectroscopic techniques. It was reported that the 3, 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. Though conducting polymers can be polymerized by two methods viz chemical and electrochemical techniques, electrochemical method offers a better control over properties as they can be tailored by changing experimental conditions [19–21] such as electrolyte, oxidation potential, solvent, etc. To date, polycarbazole is extensively synthesized using electrochemical techniques [22,23] and this polymer is mainly studied for its optical and electrochemical properties [24].

In this article, we report the electro-oxidation of carbazole (Cz) and formation of PCz, using optimum conditions, which have been

deduced from the cyclic voltammogram of carbazole in two different electrolytes and further characterized for structural, thermal and electrochemical properties.

2. Experiment

2.1. Material

Carbazole monomer and tetrabutylammonium perchlorate (TBAClO₄) and tetrabutylammonium tetrafluoroborate (TBABF₄) purchased from Aldrich Chemicals, USA. Acetonitrile (HPLC grade solvent) were obtained from Merck, India. All chemicals used were of analytical grade. Double distilled deionized water was used in all the experiments.

2.2. Instrument

Mini four probes assembly (Raman Scientifics, Roorkee, India) connected with Keithley digital multimeter and current source measurement instrument (model 2000), USA is used for conductivity measurements. Electrochemical workstation (model CHI7041C), CH-Instrument Inc., USA was used for the electrochemical characterization using three electrodes assembly. XRD measurements were carried out using 18 kW rotating anode (Cu K α wavelength 1.543 Å) based on Rigaku, Japan powder diffractometer operating in the Bragg–Brentano geometry and fitted with a graphite monochromator in the diffracted beam with 3°/min scan rate. Differential scanning calorimetry was carried out using (METTLER TOLEDO, model

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FP900 Thermosystem) at a heating rate of 10 °C/min under N₂ atmosphere.

2.3. Process of polymerization

Electrochemical syntheses and examinations were performed in a three electrode and one-compartment cell with working, counter and reference electrodes. Cyclic voltammetric (potentiodynamic synthesis of PCz) experiments was performed using platinum disc (diameter of 2 mm) and platinum gauze as a working and counter electrode by applying potential range from 0 to 1.4 V. To obtain a sufficient amount of polymer for thermal and structural characterizations, gold plate with a surface area of 10 cm² each were employed as the working as well as counter electrodes vs. Ag/AgCl reference electrode and polymer formed at 1.3 V at constant potential. Electrodes mentioned earlier were carefully polished with abrasive paper (1500 mesh), and cleaned with water and acetone successively before each examination. All potentials were referred to an Ag/AgCl electrode. The amount of the carbazole, TBAClO₄ and TBABF₄ were 60 mM, 0.1 M respectively.

3. Results and discussion

3.1. Electropolymerization of carbazole on Pt disc electrode by cyclic voltammetry

Cyclic voltammograms of PCz thin films electrochemically deposited on Pt disc electrode recorded in 0.1 M TBAClO₄ and TBABF₄ as supporting electrolytes in acetonitrile as shown in Fig. 1. The onset potentials of carbazole oxidation with TBAClO₄/ACN and TBABF₄/ACN were obtained at 0.96 and 1.05 V respectively as shown in Fig. 1. After the first cycle, the first peak intensity increased and potentials shifted toward higher values. Gradual increase in the intensity of the cathodic wave with repeated scans indicate that the product is gradually deposited on the surface of the Pt disc electrode (cf. Fig. 1). In TBABF₄/ACN solution, the anodic peaks of PCz shifted to higher potential from 0.86 to 0.91 V and cathodic peaks from 0.70 to 0.86 V to that of TBAClO₄/ACN (cf. Fig. 1) for the second cycle, probably due to difficult diffusion of ion in and out the polymer film. The cyclic voltammogram of carbazole in TBABF₄/ACN exhibited oxidation of the monomer to relatively higher potential, which affected thickness of the polymer film. The current density that was obtained for TBAClO₄/ACN which

was higher than that obtained for TBABF₄/ACN (cf. Fig. 1) supports thin and less doped state of the polymer in case of TBABF₄/ACN.

3.2. Effect of scan rate in monomer-free solution

The coated film was washed with monomer-free electrolyte solution and redox behavior was studied. Oxidation and reduction peaks were observed by increasing the applied potential for TBAClO₄/ACN and TBABF₄/ACN (cf. Figs. 2 and 3). These anodic processes are occurring at 0.86 V and 1.15 V for TBAClO₄/ACN and 0.94 V and 1.3 V for TBABF₄/ACN respectively. Such behavior may correspond to the formation of the radical cations of carbazolic units during the first oxidation step followed by their oxidation into dications through the second step [25]. Redox process is more reversible according to the I_{pa}/I_{pc} ratio in case of TBAClO₄/ACN than TBABF₄/ACN. The redox peaks are much broader and at higher potential in the case of PCz/TBABF₄ than PCz/TBAClO₄ probably because of slower ion exchange process, which collaborate to less BF₄ ions in the synthesized film. Apart from that the ion exchange also affected by texture of the film. Porosity of the film facilitates the diffusion of the ion in and out of the film [26] which supports higher porosity of the PCz film synthesized using TBAClO₄. The scan rate dependence of the electro-active film peak current was investigated on the second peak as shown in Figs. 2 and 3 (inset). The peak current (ip) for a reversible voltammogram at 25 °C is given by the following equation: $i_p = (2.69 \times 10^5) \cdot A \cdot D^{1/2} \cdot C_0 \cdot m^{1/2}$ where m is the scan rate, A is electrode area, D is the diffusion coefficient of electro-active species and C₀ is the concentration of electro-active species in the solution. Peak current was proportional to m^{1/2} in the range of scan rates which showed diffusion control process [27]. Diffusion coefficients for PCz/TBABF₄ than PCz/TBAClO₄ are 1.80 × 10⁻⁷ and 1.9010⁻⁷ respectively.

3.3. Impedance analysis

Impedance spectra of PCz films (TBAClO₄/ACN and TBABF₄/ACN) recorded in monomer-free solution at open circuit potential in the frequency range of 0.01 to 10⁴ hertz using pt disc electrode. The potential used for potentiostatic polymerization was 1.3 V for 300 s. Electrochemical impedance spectroscopy is a powerful tool for the analysis of surface treatment [28]. Apart from that ac impedance spectroscopy can be used to obtain a measure of the resistance associated with the potential specific power of the electro chemical capacitor [29]. The most important point in the impedance spectra was the resistances associated with the transport process within

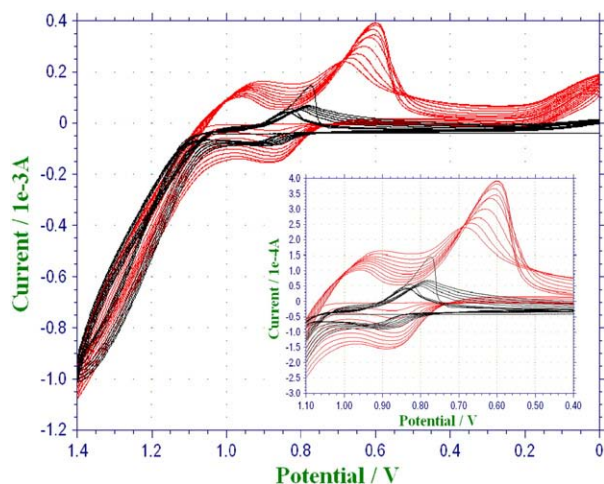


Fig. 1. Voltammogram (multisweep) of PCz in 0.1 M TBABF₄/ACN (black) and TBAClO₄/ACN (red) on Pt electrode. Scan rate: 100 mV/s. Cycles: 10 (between 0.0 and 1.4 V) [Cz] = 0.06 M.

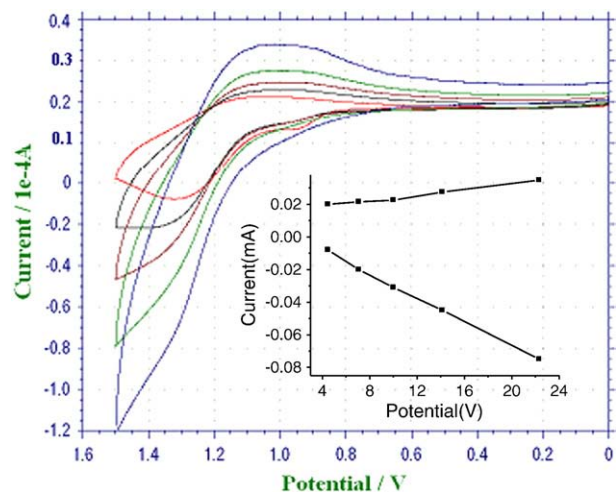


Fig. 2. Voltammogram (multisweep) of PCz in 0.1 M TBABF₄/ACN at various scan rates (from 20 to 500 mV/s) on Pt electrode. Current vs root scan rate (inset).

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