Electrochemical synthesis and characterization of a new soluble conducting polymer

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Abstract Electroactive poly(4-methyl carbazole-3-carboxylic acid) (PMCCA) film was formed on Pt electrode surface by oxidative electropolymerization of a new carbazole derivative. The structure of the soluble polymer was elucidated by nuclear magnetic resonance (^{1}H and ^{13}C NMR) and Fourier transform infrared (FTIR) spectroscopy. The average molecular weight has been determined by gel permeation chromatography (GPC) to be $M_n = 51,000$ for the electrochemically synthesized polymer. Characterizations of the resulting polymer were performed by cyclic voltammetry, dry conductivity measurement, scanning electron microscopy, and UV-vis spectroscopy. Spectro-electrochemical studies indicated that PMCCA films revealed a green color in the oxidized state and a high transmittance in the neutral state. The conductivities of PMCCA are in the range of 10^{-5}–10^{-4} S cm^{-1}.

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Introduction

Conducting polymers which can be formed electrochemically or chemically from suitable oxidizable monomers have recently attracted much attention because of a large number of potential applications. Most of these conducting polymers are not soluble in common organic solvents which make practical applications rather difficult. Since then, a number of methodologies have been developed to overcome this significant drawback [1–6]. Most common and effective ones were shown to be synthesis of self-doped conducting polymers [7] and introduction of alkyl side chains [8] in the polymer structures. It has already been stated that alkyl side chains not only improve the processability but also modify the electronic properties of the conjugated polymers [9]. The oxidation potential of the polymers [10], stability of the oxidized state [11], and band gap [12] can drastically be altered upon the insertion of strong electron-donating alkoxy side chains in the polymer backbone.

Electrochromic polymers belong to an important class of conducting polymers which are able to change color in response to electronic signals. Such polymers can be utilized in many applications like smart windows [13], displays [14], and data storing devices [15]. On the other hand, for potential application of electrochromic materials in display technologies, one should have to create the entire color spectrum and this can be only achieved by having materials with additive or subtractive primary colors in their neutral states. While a number of neutral state red and blue conjugated polymers were synthesized and their properties investigated,[16–18] attempts in making true green polymers, chemically or electrochemically synthesized, have met limited success [19–21].

The search for organic conducting polymers started in the 1970s and up to date is largely focused on polyfuran

[22], polythiophene [23], polypyrole [24], polycarbazole [25], and their derivatives. Among those polymeric structure, especially carbazole based polymer systems have attracted considerable attention over the past 30 years for the following reasons: carbazole is a cheap raw material readily available from coal–tar distillation and different substituents can be easily introduced into the carbazole ring [26, 27]. Further carbazole-containing compounds exhibit high thermal and photochemical stability. Moreover, the carbazole unit can be substituted at the 3- and 6-positions as well as at the 2- and 7-positions to provide polycarbazole derivatives with different properties and potential applications [28].

The soluble oligomers have been obtained by electrochemical polymerization of carbazole or N-substituted carbazole. The linkage of these oligomers is 3,6-positions for the N-substituted derivatives or coupled by the N,N' in the case of carbazole. As reported by Ambrose et al. [29, 30], ring–ring coupling is the predominant pathway, the carbazole radical cation yielding 3,3' bicarbazyls. But N,N' (9,9') coupling is observed for carbazole N–H. In the literature, it is accepted that the 3-, 6-, and 9-positions should be readily available as coupling sides.

One of the first reported π-conjugated polymers containing carbazole in the main chain was reported by Siove et al. [31–33]. A lot of interest in carbazole-containing polymers was caused by the discovery of photoconductivity in poly(N-vinylcarbazole) by Hoegl [34]. Their photoconductive [35] and electrochromic properties [36] promise some useful applications [37–39].

This work deals with the electrochemical properties of 4-methyl carbazole-3-carboxylic acid (MCCA) (Scheme 1) prepared recently with the aim of obtaining a new soluble conducting polymer. The synthesized electrochromic PMCCA was characterized by electrochemical and spectroscopic techniques.

Experimental

The chemical synthesis of 4-methyl carbazol-3-carboxylic acid has been previously described [40]. The procedure
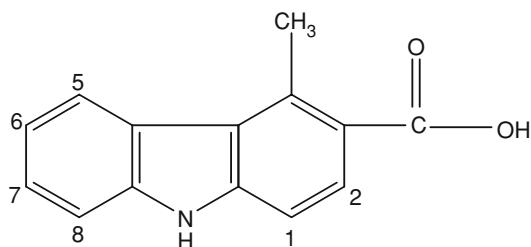
Scheme 1 The structure of the monomer

used to purify acetonitrile (Merck) has been described elsewhere [41, 42]. Tetrabutylammoniumperchlorate (TBAP) was prepared by reaction of 30% aqueous solution of perchloric acid (Analar) with 40% aqueous solution of tetrabutylammoniumhydroxide (Aldrich). It was recrystallized from ethanol–water mixture and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120 °C. Electrochemical measurements were carried out under a nitrogen (BOS) atmosphere in a three-electrode type cell with separate compartments for the reference electrode (Ag, AgCl(sat) in acetonitrile) and the counter electrode (Pt wire). The acetonitrile/0.1 M TBAP solution in the reference electrode compartment was saturated with AgCl. The working electrode which was cleaned by polishing with Al_2O_3 slurry for the cyclic voltammetric studies was a Pt disk (area, 0.0132 cm^2). The macrosamples of poly (4-methyl carbazol-3-carboxylic acid) films were prepared on a Pt macroelectrode (area, 1.0 cm^2) which was cleaned by holding it in a flame for a few minutes. The microelectrode and macroelectrode were rinsed with acetonitrile and dried before use. The films prepared electrochemically were immersed in acetonitrile to remove TBAP and soluble oligomers and vacuum dried. The pellets from the films were obtained under a pressure of 3 ton cm^{-2}. The dry conductivity values were measured using a four-probe technique at room temperature. Gold plated probes were used to avoid any errors that might arise from the ohmic contacts. At least, 10 different current values were used in the measurement of the potential drop.

The electrochemical instrumentation consisted of a PAR model 273 potentiostat–galvanostat. The current–voltage curves were recorded using a BBC Metrawatt Goertz X-Y recorder. Varian Cary 5000 UV-vis spectrophotometer was used to perform the spectroelectrochemical studies of the polymer. A three-electrode cell was utilized consisting of a silver wire pseudo reference electrode, a Pt wire counter electrode, and an ITO coated glass working electrode. The FT-IR spectra were recorded on a Varian 5000 FT-IR Spectrometer. The nuclear magnetic resonance (NMR) spectra were measured in DMSO-d$_6$ on a Bruker 400 MHz spectrometer. Scanning electron micrograph (SEM) of the polymers was performed by using Field Emission Gun Scanning Electron Microscope (FEG-SEM) (Oxford Instruments-7430). The molecular weight of the polymers was determined by Agilent 1100 GPC system with a RI detector. Tetrahydrofuran (THF) was used as the solvent and eluent in the GPC analysis.

Colorimetric measurements were achieved by a Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by CIE. During measurement, samples were placed in a light booth system where it was illuminated from behind by a D65 light source.

Results and discussion

The electrochemical oxidation of the MCCA monomer in acetonitrile/0.1 M TBAP solution was carried out to produce the polymer. Cyclic voltammetric response of a solution containing 10 mM MCCA in acetonitrile/100 mM TBAP is given in Fig. 1a. On the anodic scan, an irreversible oxidation peak at +1.15 V versus Ag/AgCl was observed corresponding to the formation of the cation radical of carbazole. Figure 1b presents the electrochemical growth of the polymer during cyclic voltammetric scan. Cyclic voltammetric response of the film between +0.0 V
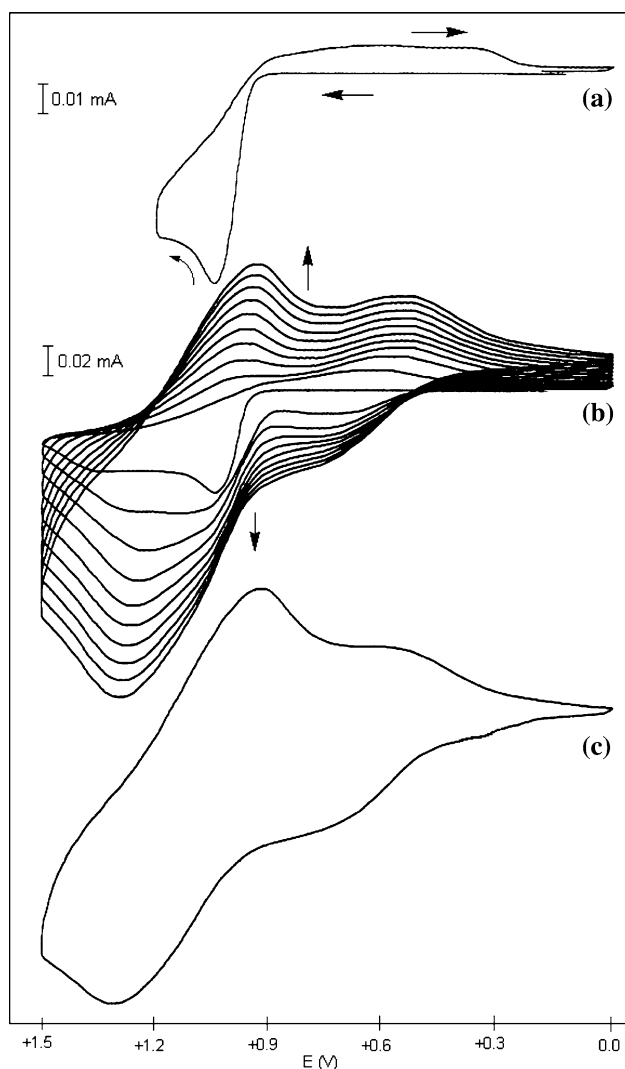
and +1.5 V Ag/AgCl show two oxidation and two reduction peaks. The film coated electrode was then transferred to monomer-free blank solution (acetonitrile/0.1 M TBAP) and the cyclic voltammogram of this coated electrode showed also two anodic and cathodic peaks (Fig. 1c). Two successive anodic peaks which were observed at peak potentials of +0.75 V and +1.3 V versus Ag/AgCl may be attributed to the formation of a cation radical (polaron) and dication (bipolaron) forms of polycarbazole.

Polycarbazole film was also synthesized at a constant potential from a solution containing 10 mM carbazole and 0.100 M TBAP. The optimum polymerization potential obtained was +1.2 V versus Ag/AgCl. At lower applied potentials the polymerization rate was lower and at higher applied potentials PMCCA film was overoxidized. The charge consumed during the deposition of the films at +1.2 V versus Ag/AgCl was 20 mC.

As shown in Fig. 2, the scan rate dependence of the polymer film was investigated between 100 and 300 mV/s. The anodic and cathodic peak current intensities of the polymer gradually increase as a function of scan rate which indicates that the films were well adhered and charge transfer process was not dominated by diffusion effects.

Spectroelectrochemical analysis of the PMCCA film was studied in order to elucidate electronic transitions upon doping of the polymer (Fig. 3). The film was deposited on ITO electrode by electrochemical polymerization of MCCA (10 mM) in the 0.100 M TBAP/acetonitrile. PMCCA coated ITO glass electrodes was investigated by UV-vis spectroscopy in the monomer free electrolytic system via switching between −0.9 V and +1.3 V. In the reduced form, at −0.9 V, the film exhibited strong absorption assigned to π–π* transitions at wavelengths below 350 nm, but it was almost transparent in the visible

Fig. 1 a The first cyclic voltammogram taken during the oxidation of 4-methyl carbazol-3-carboxylic acid in the electropolymerization solution; b multisweep cyclic voltammograms taken during the growth the polymeric film as a result of electrooxidation of 4-methyl carbazol-3-carboxylic acid; and c The blank solution cyclic voltammogram of the polymeric film which was electrodeposited from acetonitrile solutions containing 10 mM 4-methyl carbazol-3-carboxylic acid and 100 mM TBAP. Scan rate: 100 mV/s
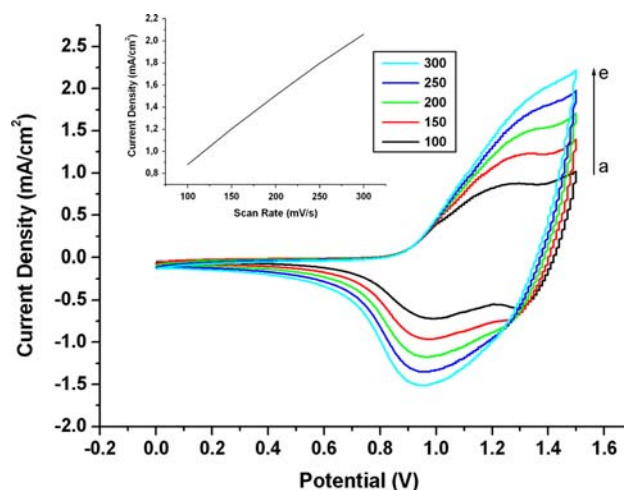
Fig. 2 Scan rate dependence of poly (4-methyl carbazol-3-carboxylic acid) film in 0.1 M TBAP/acetonitrile solution at applied potentials: a 100, b 150, c 200, d 250, and e 300 mV/s

Fig. 3 Spectroelectrochemical analysis of polymer film on an ITO coated glass slide in monomer-free 0.1 M TBAP/acetonitrile solution at applied potentials (V); **a** −0.9, **b** −0.8, **c** −0.7, **d** −0.6, **e** −0.5, **f** −0.4, **g** −0.3, **h** −0.2, **i** −0.1, **j** 0.0, **k** 0.1, **l** 0.2, **m** 0.3, **n** 0.4, **o** 0.5, **p** 0.6, **r** 0.7, **s** 0.8, **t** 0.9, **u** 1.0, **v** 1.1, and **y** 1.2
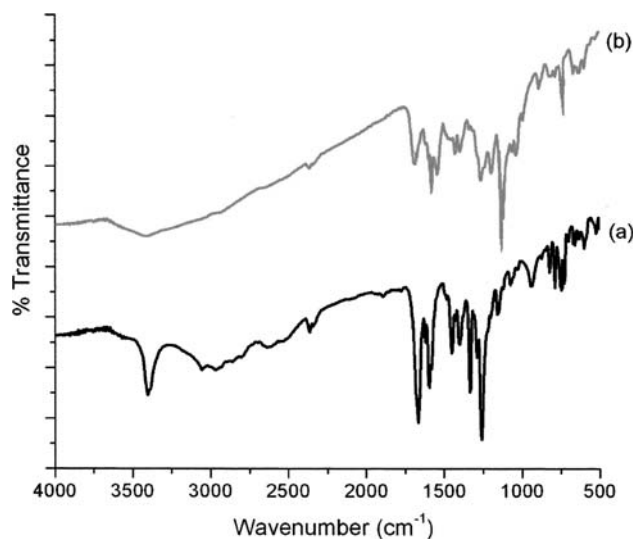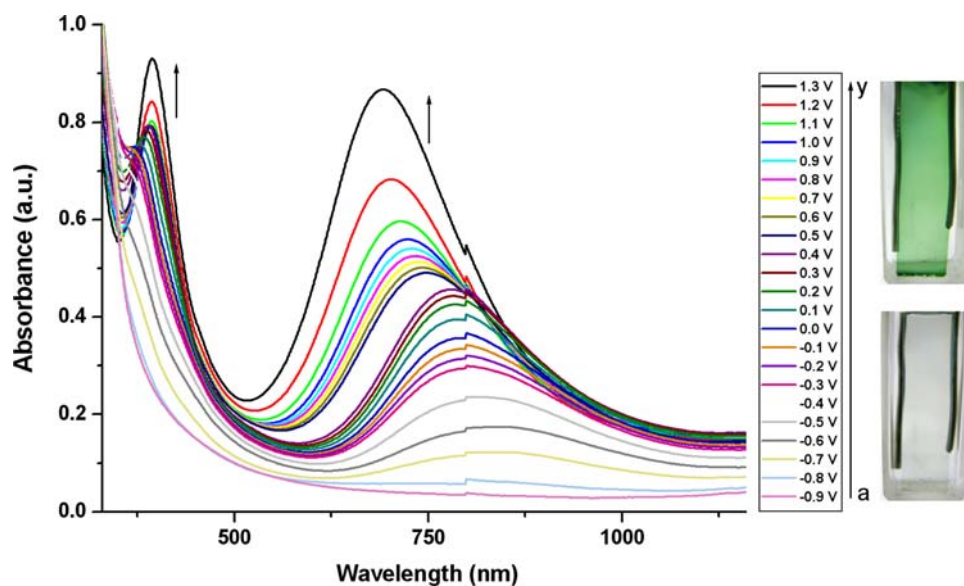

Fig. 4 FT-IR spectra of **a** 4-methyl carbazol-3-carboxylic acid, **b** poly (4-methyl carbazol-3-carboxylic acid) film which was electrodeposited from an acetonitrile solution containing 10 mM 4-methyl carbazol-3-carboxylic acid and 100 mM TBAP

region. As the applied potential became more anodic, new absorbance bands evolve at 395 nm and 690 nm due to the formation of charge carriers. The characteristic absorption peaks at 395 nm and 690 nm agree with the previously reported data of polycarbazole derivatives [43]. Spectroelectrochemistry experiments reflected a π to π* transition with a band gap energy of 3.1 eV for the polymer.

Electrochromic switching studies were carried out to obtain an insight into changes in the optical contrast with time during repeated potential stepping between reduced
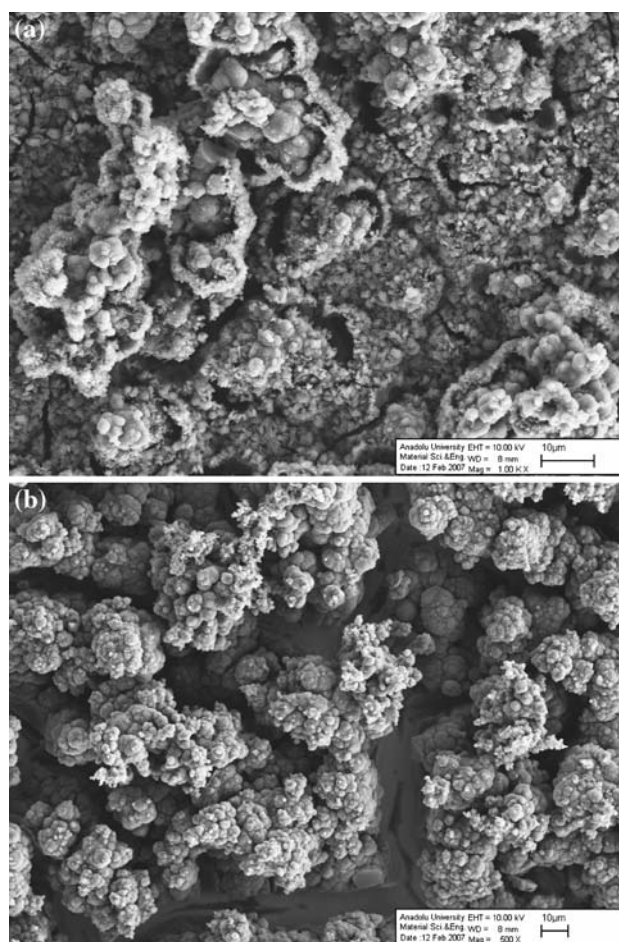

Fig. 5 Scanning electron micrographs of: **a** oxidized poly (4-methyl carbazol-3-carboxylic acid), **b** reduced poly (4-methyl carbazol-3-carboxylic acid)

and oxidized states. In these studies, the transmittance (%T) of the polymer films was recorded as a function of time at constant wavelengths. PMCCA was switched from −0.9 V to 1.3 V at 5 s step intervals in 0.1 M TBAP/ACN while the change in transmittance was monitored. The optical contrasts for PMCCA were calculated as 5% at 395 nm and 15% at 690 nm. PMCCA revealed switching times of 1.6 s at 395 nm and 2.8 s at 690 nm.

Colorimetry was used to make the measurement of the color in an objective and quantitative practice, which allows the matching of colors in electrochromic devices. The Commission Internationale de l'Eclairage (CIE) system was employed as the quantitative scale to define and compare colors. In CIE system, luminance or brightness, hue and saturation, symbolized with L, a, and b, respectively, are determined to qualify color. The PMCCA film shows different colors in the oxidized states (+1.2 V) and reduced states (−0.9 V). At the oxidized state the color of the polymer was green ($L = 76.8$, $a = -34.3$, and $b = 9.5$); on the other hand, PMCCA becomes highly transmissive ($L = 95.8$, $a = -6.2$, and $b = 9.0$) at the reduced state.

The monomer and polymer film were analyzed by FT-IR spectroscopy as shown in Fig. 4. The bands at 1118 and 625 cm^{-1} are attributed to the presence of ClO$_4^-$ ions as the dopant in the polymer structure [44]. The strong band at 1680 cm^{-1} is attributed to the presence of C=O group in the monomer and polymer. According to the FT-IR spectrum the bands present in the 1400–1650 cm^{-1} spectral range and 3415 cm^{-1} are assigned to the ring stretching vibration modes mixed with the N–H bending mode and the stretching vibration of N–H, respectively [45, 46]. After electrochemical polymerization, the band present in 3415 cm^{-1} in FT-IR spectrum of monomer disappeared and the intensity of other peak is decreased which indicates that the N,N' (9,9′) coupling occurs during the polymerization process.

Surface morphology of polymer was examined by Scanning Electron Microscopy. Figure 5 shows the scanning electron microscope pictures of PMCCA films. The morphology of the oxidized and reduced film is cauliflower-like structure.

The dry conductivity value of the oxidized polymer films synthesized at +1.2 V versus Ag/AgCl was measured

Fig. 6 ^{1}H-NMR spectra of: a 4-methyl carbazol-3-carboxylic acid, b poly(4-methyl carbazol-3-carboxylic acid) in d^6-DMSO
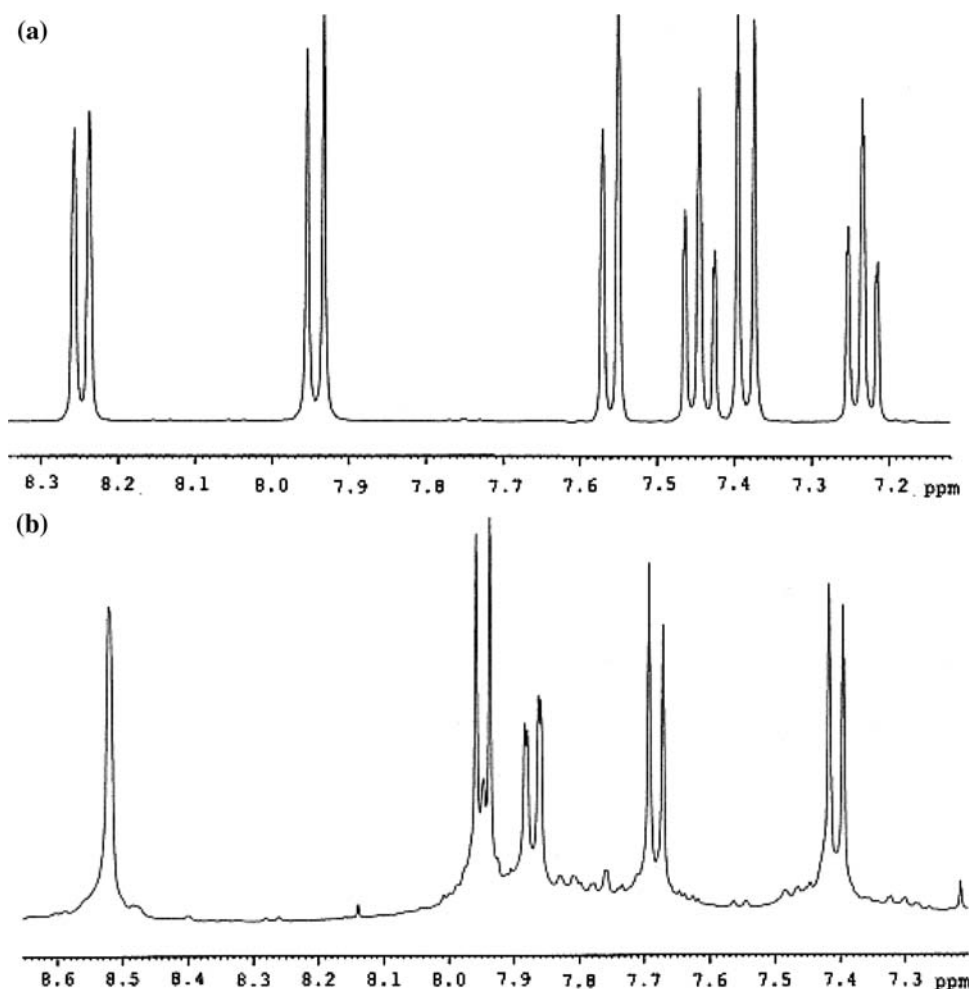
to be 1.1×10^{-4} S/cm. Conductivity values of oxidized PMCCA films which were obtained at lower and higher applied potential were found to be lower than 10^{-5} S/cm and those of the reduced film were too low to be measured.

It is known that most of the doped polymers are insoluble in common solvents. On the contrary the solubility of electrochemically synthesized doped PMCCA was found to be higher than 35 mg/mL in dimethyl sulphoxide forming a dark green solution. Moreover, PMCCA is soluble in all common organic solvents at room temperature such as CH_2Cl_2, THF, DCM, and DMF. The average molecular weight has been determined by gel permeation chromatography as $M_n = 51,000$ for the electrochemically synthesized polymer.

^{1}H-NMR and ^{13}C-NMR spectra of the doped PMCCA dissolved in d^6-DMSO were taken and compared with the spectra of the monomer in order to gain better insight about the structure of the polymer.

The 400 MHz ^{1}H-NMR spectrum of the monomer (Fig. 6a) shows a singlet at 3.12 ppm (3H, CH_3), a singlet at 11.64 ppm (1H, NH disappeared shaking with D_2O), a broad singlet at 12.43 ppm (1H, COOH, disappeared shaking with D_2O), a doublet of doublets which appears as a triplet at 7.22 ppm (1H, j: 8.13 Hz, ArH at 6 position), a doublet at 7.38 ppm (1 H, j: 7.65 Hz, ArH at 8 position), a doublet of doublets which appears as a triplet at 7.44 ppm (1H, j: 8.12 Hz, ArH at 7 position), a doublet at 7.56 ppm (1H, j: 7.60 Hz, ArH at 2 position), a doublet at 7.94 ppm (1H, j: 8.58 Hz, ArH at 1 position), and a doublet at 8.24 ppm (1H, j: 8.59 Hz, ArH at 5 position).

The 400 MHz ^{1}H-NMR spectrum of the polymer (Fig. 6b) shows a singlet at 3.22 ppm (3H, CH_3), a singlet at 11.67 ppm (1H, NH disappeared shaking with D_2O), a broad singlet at 4.46 ppm (1H, COOH disappeared shaking with D_2O), a doublet at 7.40 ppm (1H, j: 8.38 Hz, ArH at 8 position), a doublet at 7.68 ppm (1H, j: 8.32 Hz, ArH at 7 position), a doublet at 7.87 ppm (1H, j: 8.43 Hz, ArH at 2 position), a doublet at 7.95 ppm (1H, j: 8.57 Hz, ArH at 1 position), and a singlet at 8.52 ppm (1H, ArH at 5 position).

Fig. 7 a ^{13}C-NMR spectra of 4-methyl carbazol-3-carboxylic acid; b APT result of 4-methyl carbazol-3-carboxylic acid in d^6-DMSO
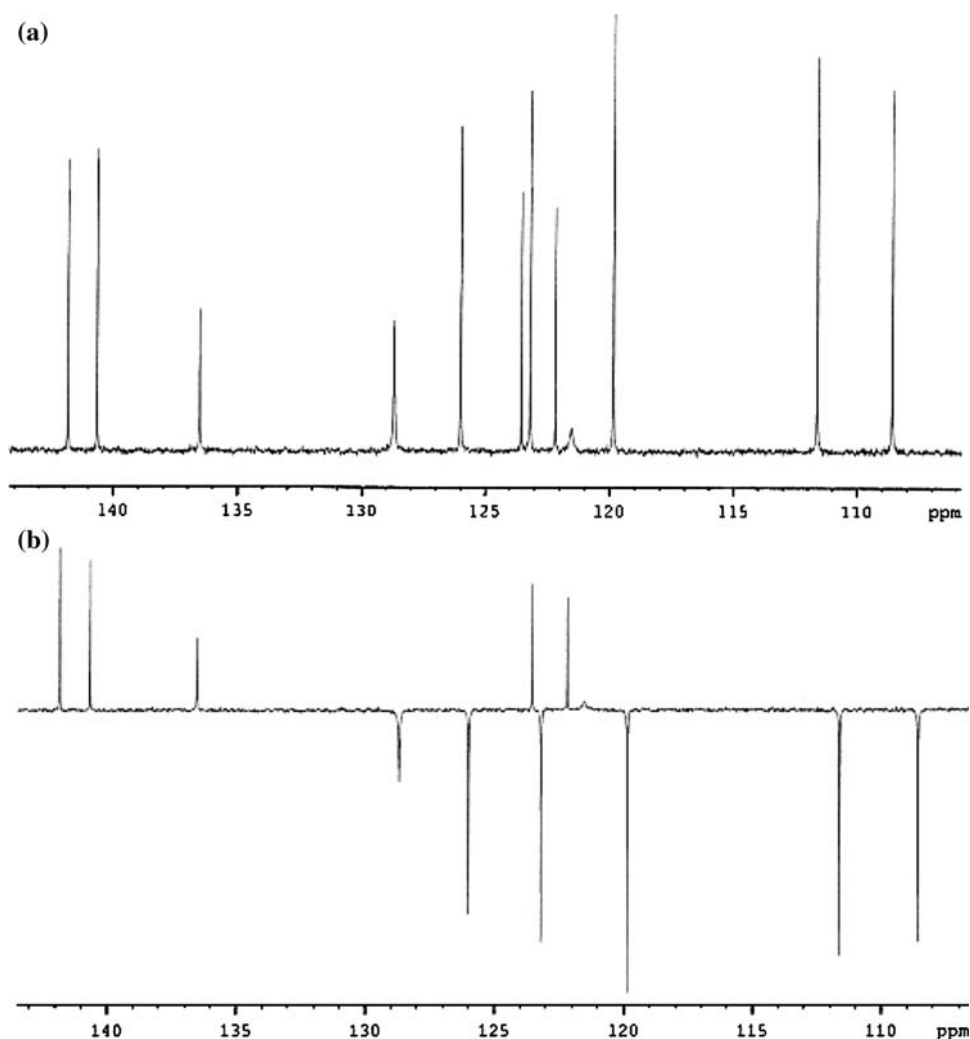
As seen from the latter ^{1}H-NMR spectrum, a doublet of doublets at 7.22 ppm which is due to the aromatic protons at 6 position of the monomer disappeared in the ^{1}H-NMR spectrum of the polymer. Furthermore the doublet of doublets at 7.44 ppm in the monomer ^{1}H-NMR spectrum appears as doublet at 7.68 ppm (ArH at 7 position) and the doublet at 8.24 ppm in the ^{1}H-NMR spectrum of the monomer appears as a singlet at 8.52 ppm (ArH at 5 position) in the ^{1}H-NMR spectrum of the polymer. These changes in the spectra imply strongly that a coupling of the carbazole rings occur at 6 position.

The 400 MHz ^{13}C-NMR spectrum (Fig. 7a) and APT (Attached Proton Test) results (Fig. 7b) of the monomer show peaks at 18.17 ppm (CH$_3$), 169.51 ppm (COOH), 108.60 ppm (CH at 7 position), 111.63 ppm (CH at 8 position), 119.87 ppm (CH at 6 position), 123.20 ppm (CH at 2 position), 126.01 ppm (CH at 1 position), 128.70 ppm (CH at 5 position), 121.53 ppm (C), 122.19 ppm (C), 123.55 ppm (C), 136.52 ppm (C), 140.66 ppm (C), and 141.83 ppm (C).

The 400 MHz ^{13}C-NMR spectrum (Fig. 8a) and APT results (Fig. 8b) of the doped polymer shows peaks at 18.29 ppm (CH$_3$), 170.01, and 169.70 ppm (COOH it is

not showed and out of range and one singlet was observed at 170.0 ppm for fully reduced polymer), 108.73 ppm (CH at 7 position), 112.04 ppm (CH at 8 position), 121.59 ppm (CH at 2 position), 125.68 ppm (CH at 1 position), 128.84 ppm (CH at 5 position), 121.61 ppm (C), 122.39 ppm (C), 124.39 ppm (C), 133.79 ppm (C), 136.78 ppm (C), 139.80 ppm (C) and 142.36 ppm (C).

There is no considerable difference of whole ^{13}C-NMR spectra of the doped and reduced PMCCA dissolved in d^6-DMSO, however, while two ^{13}C-NMR peaks (170.01 and 169.70 ppm) are observed for doped polymer, only one peak is obtained for reduced form of polymer. This difference might be attributed to two different carboxylic carbon that are carboxylic acid and carboxylate anion structure. Poly (4-methyl carbazole-3-carboxylate) acts as a counter anion (partially) in own polymeric structure (it is often called as self doped structure). Due to the fact that doping level of polymer is very low and there is an absence of carboxylate as counter anion in polymeric structure, we observed only one –COOH peak in ^{13}C-NMR for reduced form.

The peak at around 121.61 ppm in the ^{13}C-NMR spectrum of the polymer is quite intense which might be due to the overlapping of two peaks. APT results show indeed that

Fig. 8 **a** ^{13}C-NMR spectra of poly(4-methyl carbazol-3-carboxylic acid); **b** APT result of poly(4-methyl carbazol-3-carboxylic acid) in d^6-DMSO
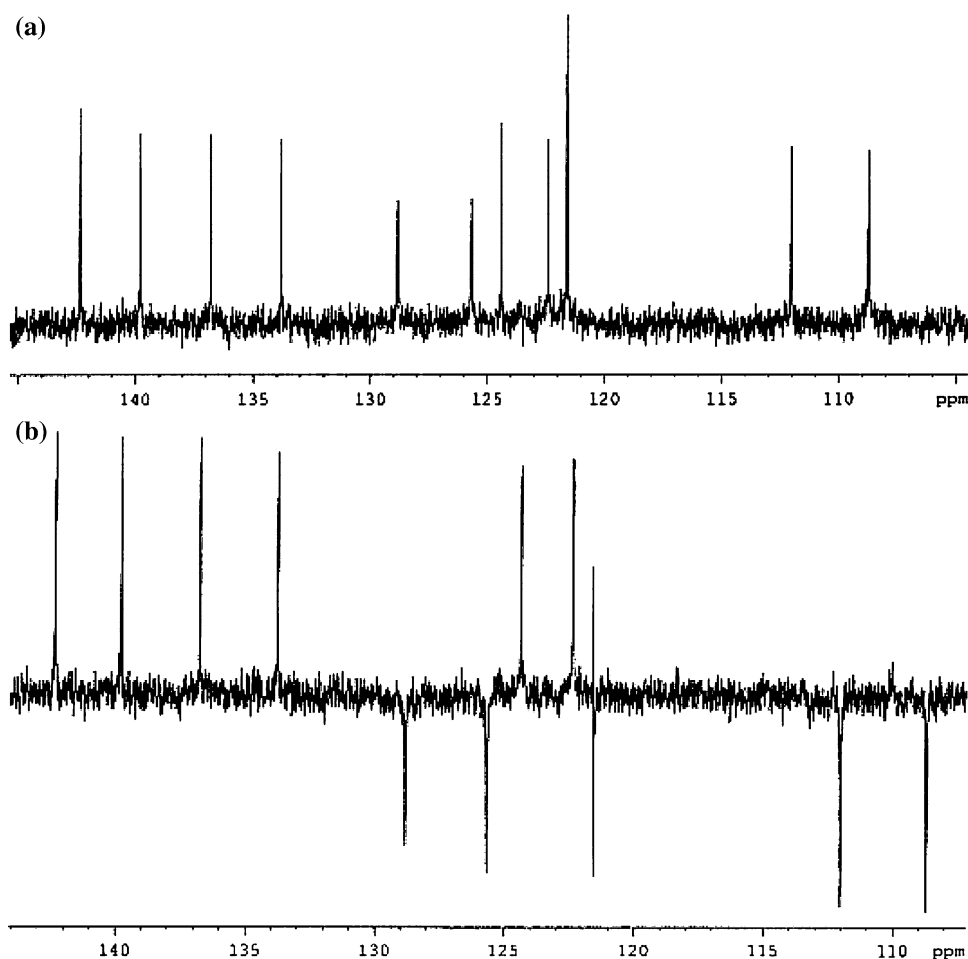
one quarterner carbon peak overlaps with the peak of a tertiary carbon in the monomer spectrum.

In general, the electrochemistry of three-substituted carbazoles is similar to that of carbazole itself. Since both the 9 (N) and 6 positions are open in these molecules one has the possibility for N–N, N-ring and ring-ring couplings [29]. When the ^{13}C-NMR spectra of the monomer and doped polymer are compared, coupling of the ring–ring is also apparent in addition to the N–N coupling. In the ^{13}C-NMR spectrum and APT results shows that there are six peaks due to quarterner carbons and six peaks due to tertiary carbons. Upon coupling of the carbazole rings there appear seven peaks due to quarterner carbons and five peaks due to tertiary carbons in the APT test.

Conclusion

After serial successive dimerization and polymerization via electrooxidation, novel self-doped polymer of 4-methyl carbazol-3-carboxylic acid is synthesized. This green colored polymeric material is soluble in DMSO due to the presence of polar carboxylic groups and conducting due to the extended conjugation and presence of the doping anion in the structure.

Spectroelectrochemical studies confirm the electrochromic properties of the films, which turn from colorless to deep green during the oxidation. In particular, by the introduction of COOH groups we can drastically improve polymer solubility and make it possible for a variety of applications such as photovoltaic and electrochromic devices.

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