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Polymer 41 (2000) 839–847

polymer

Electrosynthesis and study of carbazole–acrylamide copolymer electrodes

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Received 9 July 1998; received in revised form 18 February 1999; accepted 18 February 1999

Abstract

Polymerisation of *N*-carbazoles in the presence of acrylamide has been studied by electrochemical polymerisation onto platinum and indium tin oxide (ITO), electrodes from an acetonitrile solution of the monomers and tetraethylamonnium perchlorate-supporting electrolyte. The influence of polymerisation conditions such as electrode potential, monomer concentration, type of solvent and supporting electrolyte on the mechanical and electrochemical properties of final polymers have been studied. The redox behaviour of the polymer-coated electrodes was checked in solution containing ferrocene and dopamine solution by cyclic voltammetry. Depending on the conditions the electrode response may be reversible or quasi reversible. Cationic polymerisation of monomer is initiated either by the monomer cation radical or by the proton generated by the coupling reaction of the cation radical of carbazole. For the characterisation of copolymers Cyclic Voltammetry, UV–vis and FT-IR spectrophotometric, solid state conductivity and SEM measurements were used. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Carbazole–acrylamide copolymers; Electrocopolymerisation; Sensor materials

1. Introduction

Many heterocyclic nitrogen compounds, especially carbazole based polymer systems, can be chemically polymerised to yield materials with interesting properties. Most studies examined the chemical oxidation of carbazole [1–6] and its derivatives [7–9]. Polycarbazole (PCz) and its derivatives have been suggested for a number of applications such as redox catalyst, photoactive devices, sensors and electrochromic displays.

The π-electron system along the polymer backbone, which confers rigidity, and the crosslinking points between polymer chains, make polycarbazole insoluble, infusible and therefore poorly processable. Co-processing of polycarbazole may, therefore offer improvements in mechanical properties and processing technology. Carbazole-based polymer systems have received much attention [10–13] because of their interesting thermal, electrical and photophysical properties. Researches have continued for important properties of carbazole polymers by means of chemical modification or copolymerisation of *N*-vinyl carbazole with the other monomers [14–16]. No attempts were reported to obtain polyacrylamide (PAAm)—polycarbazole (PCz) composite or copolymer by electrochemical polymerisation.

In our studies, homopolymerisation of N-substituted carbazoles and acrylamide and characterisation of the resulting product have been investigated in detail previously [17–26], hence our choice of carbazole acrylamide is not random. It has been known that acrylamide polymers have good thermal stability and stable behaviour [27], however mechanical properties of carbazole homopolymer is weak, they show fluorescence, photoactivity and conductivity properties [28,29]. In order to test the effect of acrylamide onto carbazole structure, thermal and surface character of copolymers have been studied [30]. According to the ellipsometric and thermal (DSC) measurements of AAm–Cz copolymers which have been prepared under these conditions support the idea that optical and thermal properties of resulting copolymer have been effected by oxidation potential, reaction medium and can be improved as compared with homopolymers.

The present article deals with the incorporation of acrylamide during the polymerisation of carbazole prepared electrochemically with the aim of obtaining a new polymer, which may exhibit properties of different monomers incorporated within. Therefore, acrylamide–carbazole copolymer would exhibit the combined properties of both polycarbazole and polyacrylamide.

The electrochemical oxidation of dopamine at the polycarbazole electrode was previously examined [31,32] and exhibits semi-reversible behaviour in the buffer solution (pH = 7.35–7.40). In this study, cyclic voltametric response

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PII: S0032-3861(99)00225-6

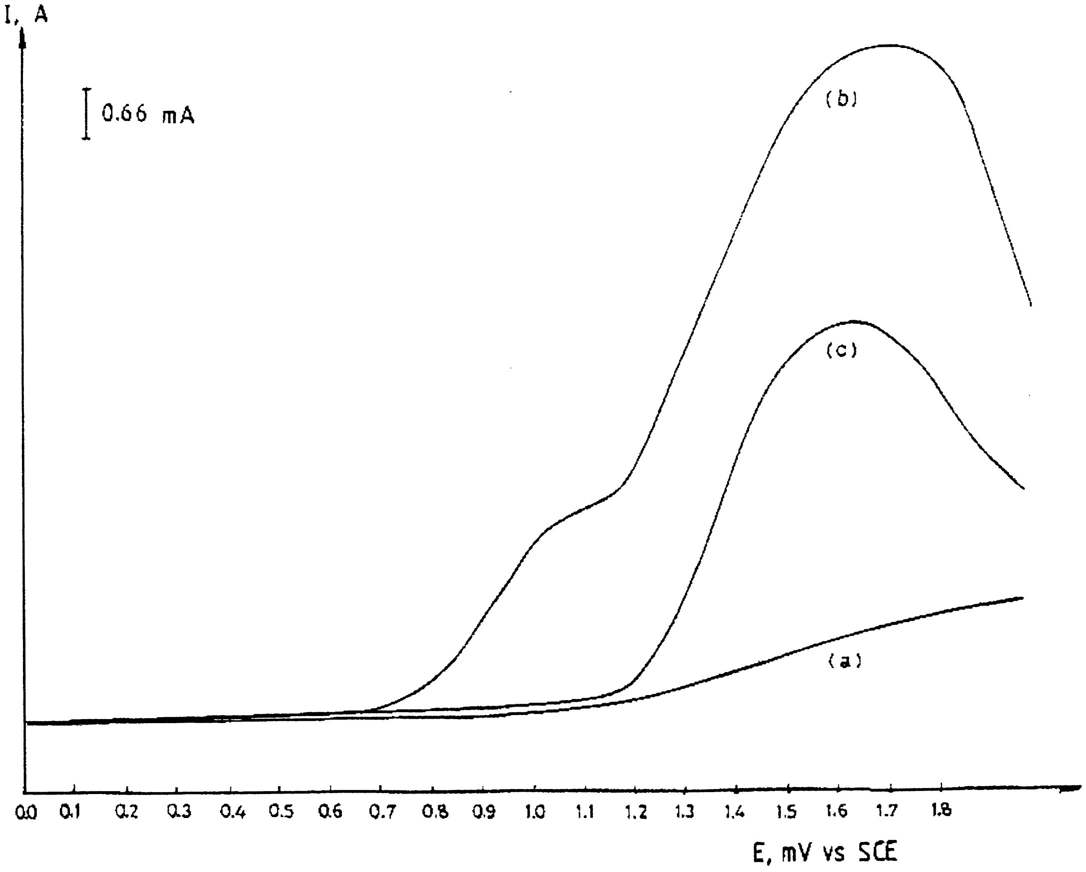


Fig. 1. Current vs. voltage of (a) 0.5 mol dm^{-3} Acrylamide, (b) 0.005 mol dm^{-3} Carbazole, (c) 0.5 mol dm^{-3} Acrylamide + 0.005 mol dm^{-3} Carbazole in the ACN solution containing TEAP, scan rate: 50 mV $^{s-1}$.

to dopamine and ferrocene was tested by prepared electrodes and compared with the literature.

2. Experimental

2.1. Materials

Carbazole (Cz, BDH), acetonitrile (ACN, Carlo Erba HPLC grade), tetraethylammonium perchlorate (TEAP, Fluka), acrylamide (AAm, Merck) were of reagent grade and used without further purification.

Phosphate buffer solutions of pH = 7 were prepared by mixing 60 ml of a 1/15 mol dm^{-3} solution of $Na_2HPO_4 \cdot 2H_2O$ with 40 ml of a 1/15 mol dm^{-3} solution KH_2PO_4 and adjusting the pH to 7 by adding either KH_2PO_4 or Na_2HPO_4.

2.2. Instrumentation

The electrochemical measurements were carried out using Wenking POS 73 Model Potentiostat connected with a Kipp and Zonen X-Y recorder. FT-IR spectra were recorded using Mattson 1000 Spectrophotometer by preparing KBr pellet. UV–visible spectra were obtained from electrochemically coated tin oxide glass and in solution by Shimadzu 160 A Recording Spectrophotometer. The SEM experiments were made on a Jeol JSM 840 Scanning Electron Microscope.

2.3. Copolymerisation

Polymerisation of carbazole in the presence of acrylamide has been grown electrochemically from solution consisting 0.1 mol dm^{-3} TEAP as a supporting electrolyte in CH_3CN. The working electrode was a Pt ($A = 0.4$ cm^2) and placed in a cell with a three electrode configuration using SCE as a reference and Pt coils as a counter electrode. In comparison, polycarbazole/polyacrylamide (PCz/PAAm) composite was also prepared electrochemically by polymerisation of acrylamide onto precoated polycarbazole.

Polarising the electrode performed electrodepositing of polymeric films by CV techniques between 0.0–1.2 V or 0.0–2.0 V (vs. SCE). Net electrodeposit on charge was recorded about 7.2×10^{-2} C. Polymerisation occurred at the anode surface. The changes in the solution were also investigated by UV–vis spectrophotometric measurements simultaneously. The films obtained on the electrode surface were washed with ACN and water several times to remove

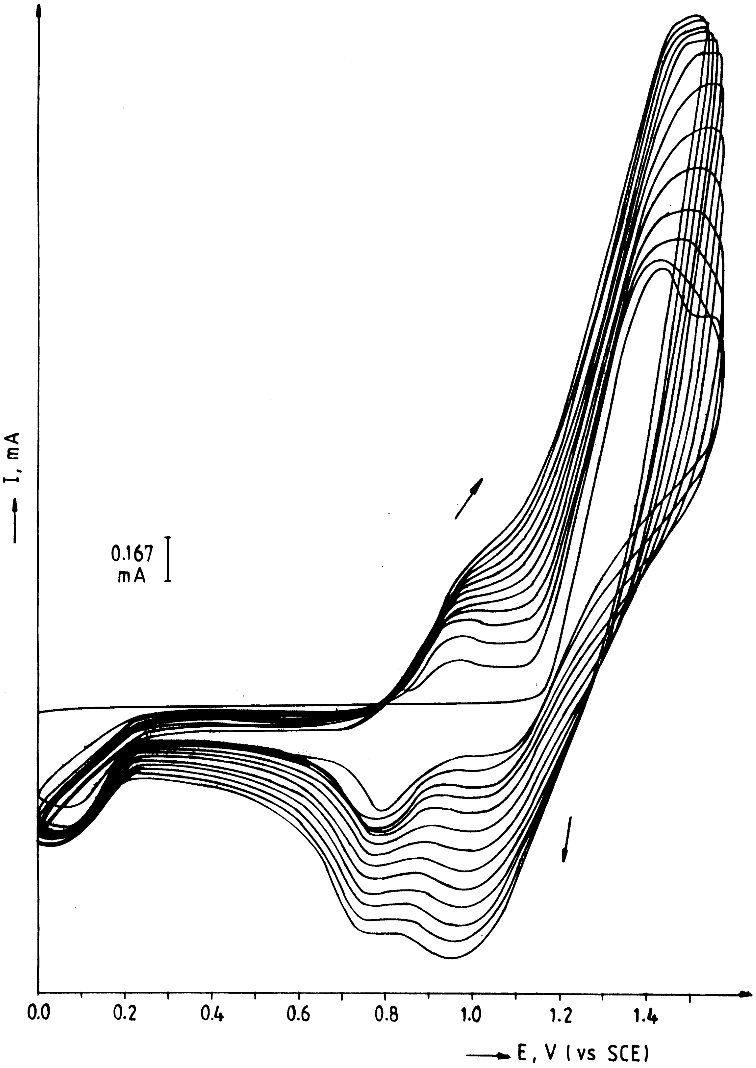


Fig. 2. Cyclic Voltamogram of 0.01 mol dm^{-3} Carbazole electrochemically deposited onto Pt in the ACN solution containing 0.1 M TEAP as a supporting electrolyte, scan rate: 100 mV $^{s-1}$.

the unreacted monomers and homopolymers. After polymer deposited onto platinum, it was left in vacuum for 48 h. The response of coated electrodes to dopamine (0.018 mol dm^{-3}) and ferrocene (0.004 mol dm^{-3}) were tested in the buffer solution ($pH = 7.10$) and in 0.1 mol dm^{-3} TEAP containing acetonitrile at different scan rates. The stability of electrodes were tested by leaving them in 0.1 mol dm^{-3} H_2SO_4 and acetonitrile solution for different time intervals. The filmed electrodes were tested by CV in a cell of the same configuration.

Solid state conductivity measurements were performed on the pressed discs at room temperature on a Keithley 617 Electrometer connected to a four probe head with gold tips and calculated from the following equation [33]:

$$\sigma = I \times V^{-1}(\ln 2/\pi d)$$

where, V the applied potential, I is current, and d the thickness in cm.

3. Results and discussion

3.1. Current–potential curve during the preparation of copolymers

Current–potential curve during the incorporation of AAm into Cz strategy employed in the present study was to oxidize carbazole under diffusion limiting conditions. For this purpose carbazole with a concentration as low as 5×10^{-3} mol dm^{-3} was chosen, while that of acrylamide was set at 0.5 mol dm^{-3} due to which the rates of polymerisation of each monomer become comparable and might allow copolymerisation. When the amount of carbazole was increased, mainly polycarbazole homopolymer was obtained. Current–potential curve was taken in these solutions at a potential swept rate 50 mV $^{s-1}$ are given in Fig. 1. The curve (a) concerns a current–potential curve for electropolymerization of acrylamide, curve (b) for carbazole and curve (c) for carbazole–acrylamide. Curves (a) and

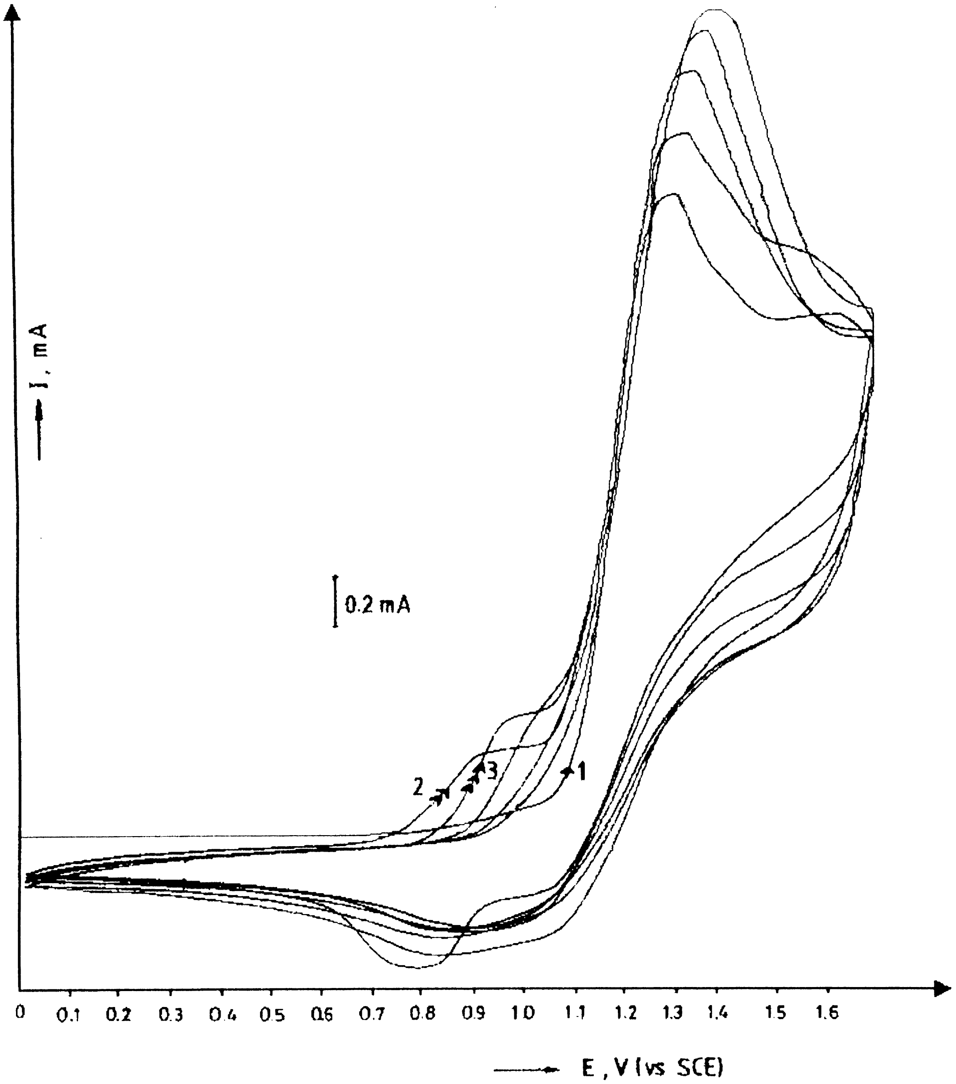


Fig. 3. Repeated scan polymerisation of 0.01 mol dm^{-3} Carbazole and 0.5 mol dm^{-3} Acrylamide monomers electrochemically deposited onto Pt in the ACN solution containing 0.1 M TEAP as a supporting electrolyte, scan rate: 50 mV $^{s^{-1}}$. 1, 2, 3 show first, second and third cycle.

(b) add up to make the curve (c) supporting copolymerisation takes place in these conditions.

3.2. Cyclic voltammetry

The cyclic voltamogram of carbazole in acetonitrile exhibits only one oxidation wave (Epa: 1.43 V vs. SCE) in the first sweep, but the corresponding cathodic wave is very weak in intensity, a new band appearing instead (Fig. 2). However when the sweep is repeated, the cyclic voltamograms show two anodic wave (Epa: 0.95 V vs. SCE and Epa 1.42 V vs. SCE) and the corresponding cathodic waves and the oxidation process tends to show reversible characteristic peaks. The gradual increase in the intensity of waves with repeated sweeps indicates that the reaction product is gradually deposited on the surface of the electrode.

The first and second anodic waves are ascribed to the oxidations of the 3,3′ bis carbazole and the isolated carbazole moieties, respectively. It is suggested that the cationic polymerisation of monomers is initiated either by the monomer cation radical or by the proton generated by the coupling reaction of cation radical of the carbazole.

There are some differences in CV of Cz in the presence of AAm in the oxidation direction. By repeated cycles (Fig. 3; cycles 1–3) shift in anodic peak as well as absence of reverse peak in cathodic direction indicate the reaction between Cz and AAm. In the first sweep (cycle 1) oxidation of carbazole to cation radical takes place and cathodic peak corresponds to its reduction. In the second sweep, cation radicals react by acrylamide. Upon multiple cycling of the solution a new peak develops at a lower potential ($E_a = 0.880$ V, cycle 2) due to deposition of electroactive product on the surface of the working electrode. By increasing repeated cycles peak shift to the more anodic direction due to reaction by acrylamide. This result let to a conclusion of a different polymeric film formation in accordance with

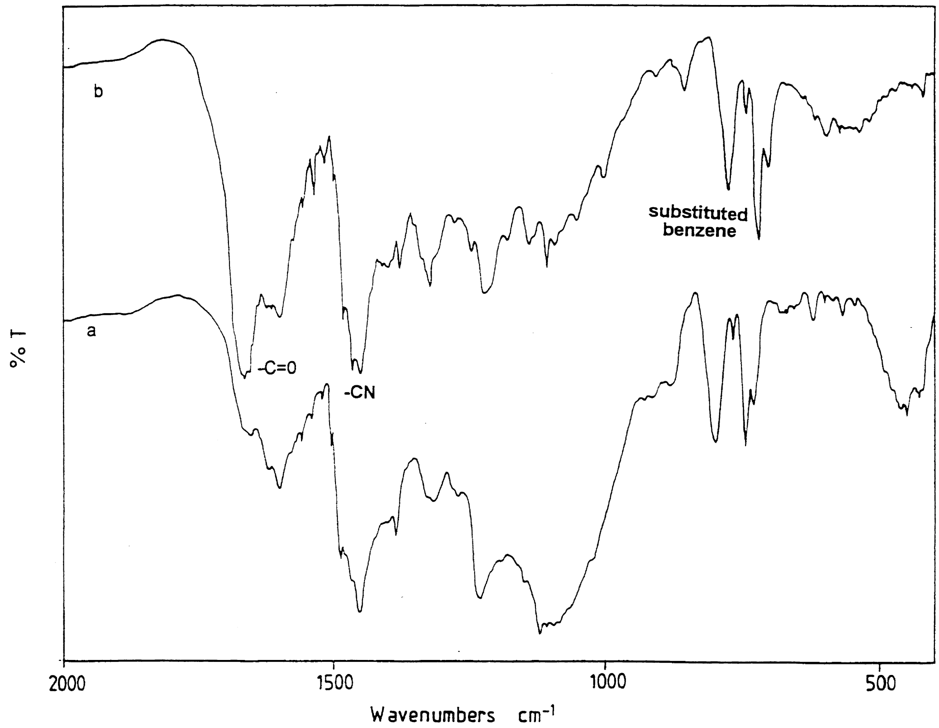


Fig. 4. The FT-IR spectra of (a) Composite, (b) Copolymer, $n_{\mathrm{AAm}}/n_{\mathrm{Cz}} = 50$, applied potential: 1.2 V.

the homopolymer of carbazole occurred at the surface. Further evidence for the formation of the polymer is the observation of a light green film on the surface.

3.3. FT-IR measurements

The carbazole monomer has bands at 3550, 1620, 1450, 1350, 1280, 940, 760 and 440 cm^{-1}. The spectral features agree with the previously reported data [34,35]. When the carbazole monomer was electropolymerised it gives bands at 1100 and 620 cm^{-1}, which is attributed to $\mathrm{ClO_4^-}$ [36] and the bands in the range 750–900 cm^{-1} which correspond to 1,2,4, substituted benzene ring appears in the FT-IR spectrum.

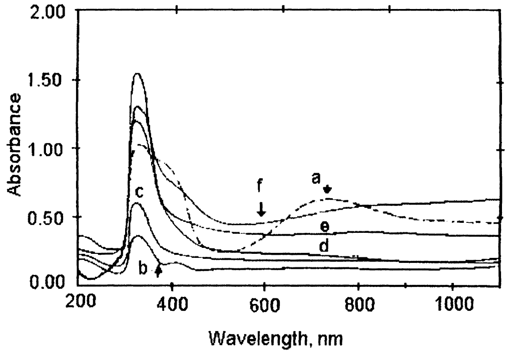


Fig. 5. UV–visible spectra of electrochemically prepared (a) polycarbazole film, (b) acrylamide/carbazole copolymer ($n_{\mathrm{AAm}}/n_{\mathrm{Cz}} = 10$) film on ITO, and changes by increasing reaction time (b)–(f) at the 1.2 V applied potential in ACN. Curves were collected within time intervals at 2 min (a), 5 min (b)–(f).

Polymerisation by comonomer performed at two different potentials (1.2 and 2.0 V) and different AAm/Cz (100 and 400) mole ratios. Applied potential shows no significant effect on the copolymer structure. In the FT-IR spectrum of the resulting polymers obtained both at 2.0 and 1.2 V, the band at 1650 cm^{-1} which is attributed to the –C=O group of AAm appears, and the intensity of this band increase with increasing AAm feed, showing incorporation of AAm into the structure. In addition to this, –C=O band at 1650 cm^{-1} increase in the intensity of bands at 1453 cm^{-1}, which correspond to –C–N and bands at 805 and 750 cm^{-1} which correspond to the substituted benzene ring, by increasing the AAm feed, also support the idea mentioned earlier. Therefore, the presence of the band at 3550 cm^{-1}, which is attributed to –NH str. and disappearance of the band at 1550 cm^{-1} which is due to aromatic –CH of carbazole ring in the presence of acrylamide show that polymerisation goes through the Cz ring.

In order to understand the type of incorporation of AAm into the final polymer, the copolymer formed at the mole ratio of $n_{\mathrm{AAm}}/n_{\mathrm{Cz}} = 50$, and the composite was compared in accordance with their FT-IR characteristic. The final product dissolved in water to remove PAAm that might be formed on the upper side of the composite and may occur in the copolymer structure. It can be seen from the FT-IR spectra of these polymers (Fig. 4(a) and (b)), the intensity of the band at 1650 cm^{-1}, which is attributed to the decreasing –C=0 group of acrylamide. As the PAAm was dissolved

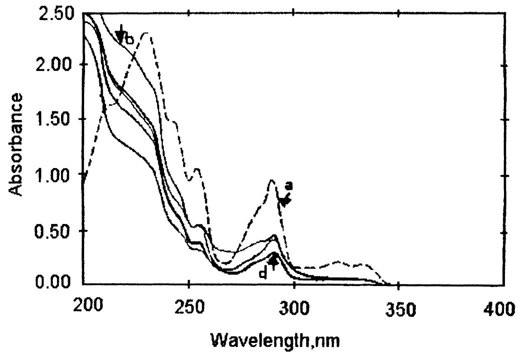


Fig. 6. UV–visible spectra of 0.01 mol dm^{-3} Carbazole (a), and changes in the absorption spectra of reaction solution obtained during copolymerisation at $n_{AAm}/n_{Cz} = 20$ and 1.2 V applied potential by increasing the time (b)–(d). Each curve corresponds to five minutes interval.

in water, washing the composite caused a change in the structure (Fig. 4(a)). While by washing with water, there is no change at the same band for the copolymer (Fig. 4(b)), which supports the possibility of copolymerization of AAm with Cz.

3.4. UV–visible measurements

Fig. 5(a) shows the UV–visible spectra of perchlorate doped polycarbazole on ITO (Indium Tin Oxide). The characteristic absorption peaks such as those at 738, 400 and 350 nm agree with the previously reported data [37,38].

In the presence of AAm the decrease in the intensity of 738 nm peak due to a decrease in the number of redox sites might be ascribed to the coexistence of AAm groups with Cz (Fig. 5(b)). Increase in the intensity of this peak can be attributed to the enhanced concentration carbazole radical ions formed because of the increased polymerisation time (Fig. 5(b)–(f)).

In addition to the film, which occurred at the anode surface (ITO), reaction in the solution was also followed spectroelectrochemically by UV–vis measurements. The characteristic peaks of the carbazole at 231, 260, 291, 321 and 340 nm (Fig. 6(a)) shift and the intensity of peak at 290 nm decrease in the presence of acrylamide ($n_{AAm}/n_{Cz} = 20$), (Fig. 6(b)). The intensity of the characteristic peaks of carbazole decrease with increasing reaction time (Fig. 6(b)–(d)) showing the incorparation of the AAm into the Cz structure.

3.5. Morphology of polymers

In order to understand the surface appearance of the copolymer film coated on platinum Scanning Electron Microscopy (SEM) was used. The SEM for the electrochemically oxidised final polymers and polycarbazole film in ACN are shown in Fig. 8. For the copolymer carbon paste was used as a substrate for the analyses. Polycarbazole has been known as it shows a cauliflower-like structure [39]. The SEM microphotographs of the electrochemically prepared polymers show structurally different morphology (Fig. 7(a)). At a higher magnification clusters of globules with void space in between can be seen clearly. Fig. 7(b), indicates the incorporation of AAm into the resulting structure.

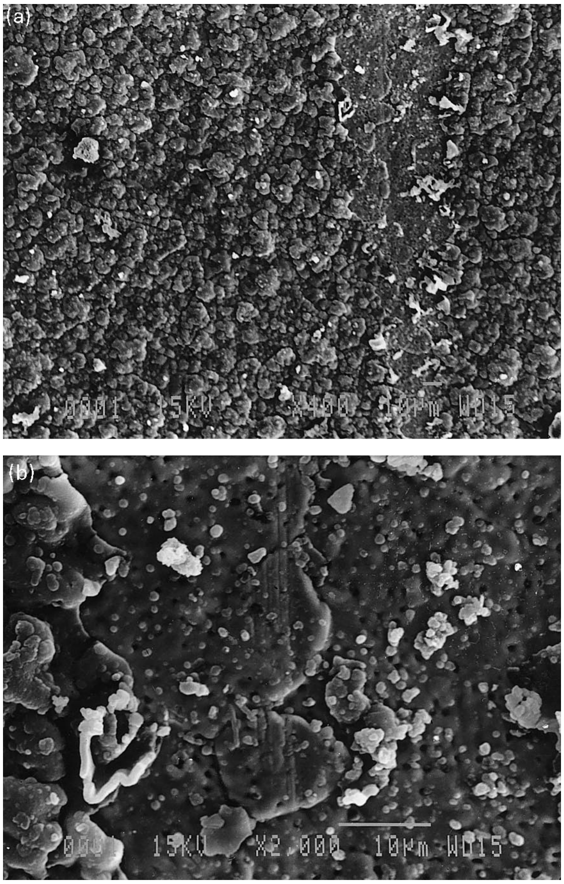


Fig. 7. Scanning electron micrographs of acrylamide/carbazole copolymer ($n_{AAm}/n_{Cz} = 50$) at different magnifications, × 400 (a) and × 2000 (b).

3.6. Conductivity measurements

The solid state conductivities of the proposed copolymers and the composites are given in Table 1. The electrocopolymerisation of carbazole derivatives with AAm cause some decrease in the conductivities as expected. In the presence of PAAm in composite structure also has a negative effect on the conductivities of the composite. Decrease in the conductivity in the case of the copolymer and the composite suggests the interaction between Cz and AAm. When $n_{AA}/n_{Cz} = 1$ conductivity of the copolymer is almost the same with the homopolymer of polycarbazole as in this case copolymer formation is less possible due to kinetic reasoning.

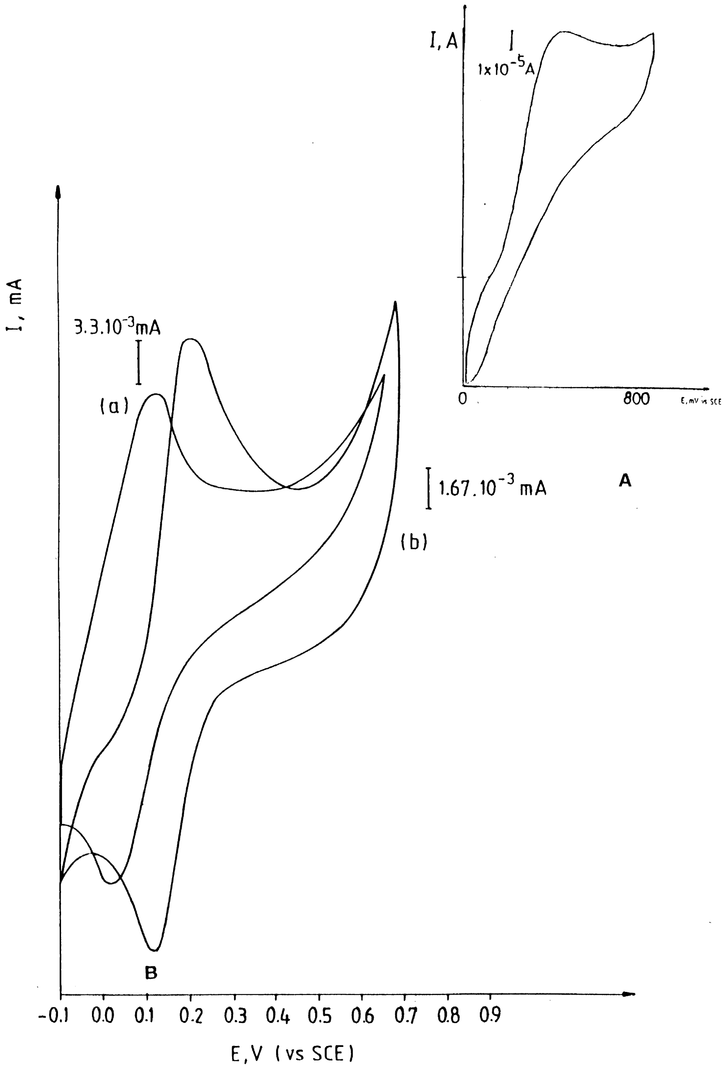


Fig. 8. Cyclic voltamograms obtained for 0.018 mol dm^{-3} dopamine in buffer solution (pH = 7.4); (A) at the Pt electrode, (B) acrylamide/carbazole copolymer (n_{AAm}/n_{Cz} = 50) electrode, (a) newly prepared electrode, (b) after three days, scan rate: 50 mV $^{s-1}$.

3.7. Yield of polymers

An increase in the applied potential and the carbazole–acrylamide mole ratio results in an increase in the copolymerisation yield (Table 2). In the FT-IR spectra of copolymers, increase in the intensity of the band at 1650 cm^{-1} due to the –C=O group of acrylamide supports the idea that increase in yield is due to the incorporation of acrylamide into the structure.

Table 1
Conductivity of polymers

Polymer (n_{AA}/n_{Cz})	Conductivity (S/cm)
Composite	1.27×10^{-6}
50 (Copolymer)	1.84×10^{-6}
1 (Copolymer)	3.6×10^{-2}
Polycarbazole	1.3×10^{-2}

By the addition of 2.8×10^{-4} mol dm^{-3} water, only minor alteration in the yield can be detected at 1.2 V applied potential, the highest yield can be obtained at n_{AAm}/n_{Cz} = 400 mol ratio (Table 2) in the case of higher applied potential. Observation of the highest intensity of the –C=0 band at 1650 cm^{-1} at 2.0 V applied potential in the presence of water also supports the above mentioned idea.

3.8. Response of the copolymer electrodes to ferrocene and dopamine

For understanding the redox properties of the film, a current voltage curve is recorded. The polymeric film reveals only one anodic peak at about 0.80 V and one cathodic peak at 0.88 V. The intensity of the peak increases by an increase in the scan rate suggesting that the electron transfer reaction is fast.

Table 2
Effect of AAm to Cz mol ratio applied potential and water on the copolymerisation yield, supporting electrolyte: TEAP, temperature: 20°C

n_{AAm}/n_{Cz}	Reaction medium	Applied potential (V)	Yield (%)
100	ACN	1.2	3.0
400	ACN	1.2	4.2
100	ACN	2.0	Trace
400	ACN	2.0	5.1
100	ACN–H_2O[a]	1.2	6.0
400	ACN–H_2O[a]	1.2	5.0
100	ACN–H_2O[a]	2.0	1.7
400	ACN–H_2O[a]	2.0	8.6

[a] $H_2O = 2.8 \times 10^{-4}$ mol dm^{-3}.

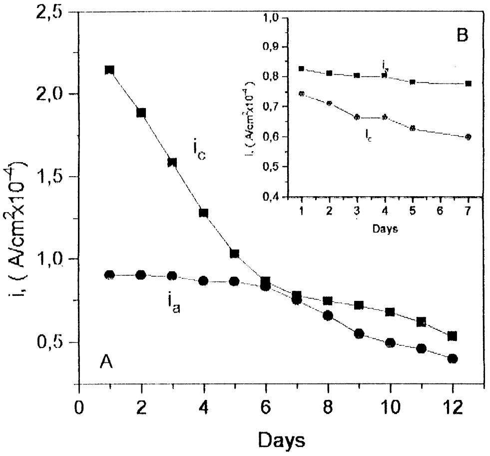


Fig. 9. Changes in anodic (I_a) and cathodic (I_c) peak current response of copolymer electrode to ferrocene lefted, (A) in ACN during 12 days; (B) in 1 mol dm^{-3} H_2SO_4 medium during seven days, supporting electrolyte: TEAP, [ferrocene] = 0.004 mol dm^{-3} scan rate: 50 mV $^{s-1}$.

As the cyclic voltammetric measurements show the response to dopamine at platinum, Cz–AAm copolymer electrode in the phosphate buffer of pH = 7.35 in the presence of 0.018 mol dm^{-3} dopamine are prepared (Fig. 8(A) and (B)). In the case of Pt electrode, an irreversible behaviour was observed (Fig. 8(A)) as given in literature [34]. According to the voltammetric measurements shown in Fig. 8(B), polymer obtained in the presence of AAm electrode, redox process ($E_a = 0.15$ V, $E_c = 0.025$ V) can be distinguished for a solution of dopamine in buffer and the reversibility of copolymer electrode (Fig. 8(B) curve a) showed better behaviour than the naked Pt (Fig. 8(A)).

The stability of the polymer electrode was tested by leaving the electrode in vacuum for three days, and CV of the electrode was taken at different time intervals. During this time, the intensity of the peak currents decreased and anodic shift in the peak potential occurred. After three days the electrode became almost stable and no shift was observed in the peak potential. The CV of the electrode left for three days in vacuum is given in Fig. 8(B) curve b.

The copolymer electrode seems to respond very significantly to dopamine and remained stable after three days (Fig. 8(B)).

The electrochemical oxidation of dopamine at the prepared polymer electrode was also examined as a function of sweep rate 0.05–0.2 V s^{-1}. As it is expected, the intensity of the peak current increases with increasing sweep rate. It is known that for the polycarbazole electrode, peak separation is quasi-reversible at slow sweep rate [32]. In our case even at slower rate, it is possible to obtain reversible peak response, which exhibits the advantage of the polymer electrode synthesized in this way.

These results suggest that the electrode responds in a reproducible manner and this electrode is sensitive and has reversible behaviour.

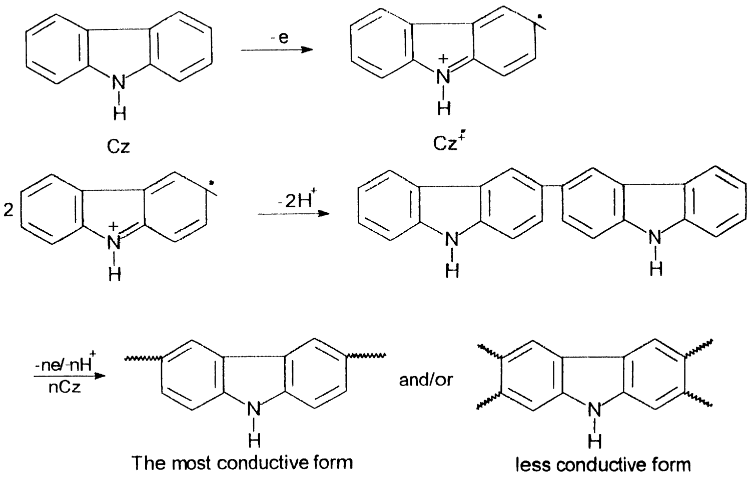
The electrode response to ferrocene was also tested by CV measurements. The anodic ($E_a = 0.48$ V) and the cathodic peak potential ($E_c = 0.39$ V) show a slight shift to the anodic direction in the case of the copolymer electrode in comparison to the naked Pt ($E_a = 0.44$ V, $E_c = 0.37$ V). The copolymer film represents reversible behaviour in the presence of ferrocene.

The reproducibility of the current response of the polycarbazole–acrylamide electrode for sensing ferrocene was assessed by recording the cyclic voltammetric responses everyday for a period of 15 days, the electrode was left in ACN and 1 mol dm^{-3} H_2SO_4 after each day. Fig. 9(A) and (B) show the plot of current densities response as a function of time. When the electrode is initially left in ACN, the cathodic current shows a decreasing trend, and becomes almost constant after four days (Fig. 9(A)). Later, there is less change in the anodic current densities. In addition to these experiments, the electrode was left in 1 mol dm^{-3} H_2SO_4 and the anodic and cathodic peak current densities of the copolymer electrode in the presence of ferrocene were recorded (Fig. 9(B)). The current densities almost become constant at the end of seven days, indicating that the stability of the electrode is better under these conditions.

4. Conclusion

Our previous study on thermal measurement (DSC) and ellipsometric results [30] and the results of this study suggest that at certain mole ratio of AAm/Cz can give considerable amount of new polymer. This polymer shows different physical and chemical properties than composite structures with a still some possibility of electrostatic and other types of strong interactions. Such copolymeric structure behaves in a reversible manner in the presence of ferrocene and dopamine.

According to our results, we can suggest a tentative mechanism, in addition to the known Cz oxidative coupling reaction as follows:



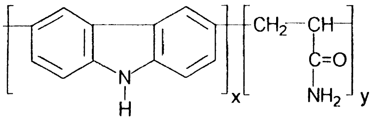
Polycarbazoles (PCz)

The electrochemical polymerisation takes place via -3 and/or -6 position of the carbazole ring, as this position is the most reactive. However, polymerisation via the other position is also possible resulting in less conductive form of the polymer. In the presence of AAm, cation radicals may react after nucleophilic substitution with AAm, resulting polymer.

$$(\mathrm{Cz})_n^{+\bullet} \xrightarrow{\mathrm{Nu}^-} \mathrm{Nu}\text{-}(\mathrm{Cz})_n^{\bullet} \xrightarrow{\mathrm{AAm}} \text{Polymerization}$$

where $\mathrm{Nu}^- =$ solvent or AAm itself and $n = 1$ or $n > 1$.

Probable copolymer structure may be as follows:



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