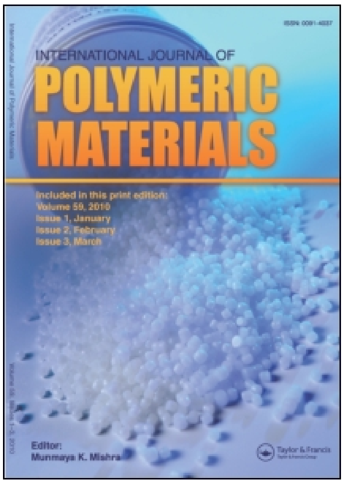

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N-VINYLCARBAZOLE-STYRENE FREE RADICAL POLYMERIZATION AND ELECTROCHEMICAL AND CHEMICAL OXIDATION OF P[NVCZ-CO-STY] AND P[NVCZ-CO-AN]: CYCLIC VOLTAMMETRIC, SPECTROSCOPIC (FTIR), AND CONDUCTOMETRIC STUDY

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N-VINYLCARBAZOLE-STYRENE FREE RADICAL POLYMERIZATION AND ELECTROCHEMICAL AND CHEMICAL OXIDATION OF P[NVCz-co-STy] AND P[NVCz-co-AN]: CYCLIC VOLTAMMETRIC, SPECTROSCOPIC (FTIR), AND CONDUCTOMETRIC STUDY

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Poly(N-vinylcarbazole-styrene) (PNVCz-St) and Poly(N-vinylcarbazole-acrylonitrile) (PNVCz-AN) were synthesized by the reaction of ceric ammonium nitrate (CAN) in acetonitrile and the resulting products are oxidized chemically or electrochemically. Electrochemical coating of random copolymers of P(NVCz-St), P(NVCz-AN) were performed on Pt that by using polymers that were prepared by free radical polymerization with Ce(IV). The resulting products were characterized by 4-point probe conductivity measurements and cyclic voltammetry (CV) and Fourier transformed Infrared Spectroscopy (FT-IR).

Keywords: polymerization, N-vinylCarbazole, styrene, electrochemical oxidation

1. INTRODUCTION

A great deal of attention has been paid to Poly(N-VinylCarbazole) (PNVCz) over the years because of its unusual electrical and photoelectrical properties. It has been suggested for a number of applications, photoactive devices, sensors and electrochoromic devices [1]. The common usage of PNVCz material has been restricted due to its poor processibility and lack of stability [2]. It should be emphasized that NVCz is not polymerized only through the benzene ring but also through vinyl groups [3].

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The preparation of PNVCz by electrochemical polymerization has been known for many years [4–5]. The first stage of electropolymerization involves the oxidation of the monomer to a cation radical. Then, depending on the electrochemical conditions, several pathways of polymerization are possible and in consequence, the obtained films reveal different structures and properties [6]. The electrolysis of N-vinylcarbazole (NVCz) solution usually results in a coating on the anode surface with a green conducting polymer. Besides this, in the bulk of the solution the formation of the nonconducting colorless PNVCz, in which the polymer chain is formed exclusively by bonds between vinyl groups is also possible [7–8].

In spite of the great interest in the electrochemical preparation of PNVCz, the oxidative polymerization of NVCz in nonaqueous systems, using metal ion oxidant, i.e., Cerium (IV), has not been studied systematically. Wang [9] presented the first report on the polymerization of NVCz initiated by oxidizing nitrates in methanol. According to him, ceric ammonium nitrate, ferric nitrate and cupric nitrate are capable of polymerizing NVCz in methanol solution and also of polymerizing compeletely the mixture of NVCz and styrene [10–11]. Such metal salts can accept electrons leading to oxidation of NVCz during which radical ion might be formed as an intermediate. The polymerization of NVCz in ethylene dichloride, acetone, benzene and dioxane with cupric nitrate, ferric nitrate, and ceric ammonium nitrate catalysts was studied. In all of these cases, polymerization seemed to be cationic in type and yields are around 20%–50% for ceric ammonium nitrate (CAN) in 2 hours [11].

Oxidative polymerization of NVCz was studied with CAN [12]. Due to its clean stoichoimetry and strong oxidizing power, Ce(IV) has been used recently in the polymerization of vinyl monomers [12–14], pyrole in acetonitrile [15] and in the polymer matrix [16]. Poly(vinylcarbazole) in solution can show high electrical conductivies when suitable ratio of oxidant/monomer is selected [13]. The results indicate that the reaction proceeds by a different route depending on the CAN concentration. If CAN concentration is 5 times lower than the monomer concentration, a colerless polymer is formed, indicating the polymerization proceeds through the vinyl groups. When the concentration ratio is higher than this value, polymerization proceeds from benzene rings forming green dark polymers.

Sarac et al. [17] indicated that in the Ceric salts initiated vinyl polymerization, both ceric ions and primary free radicals participate in the initiation process while termination occurs exclusively by interaction of propagating chain radicals and ceric ions or mutual combination of growing chain.

In our previous study, polymerization of NVCz in the presence of Acrylamide (AAm) has been studied by electrochemical polymerization onto Pt and indium tin oxide (ITO) from acetonitrile solution of monomers and using tetraethtyl ammonium perchlorate (TEAP) as supporting electrolyte [18]. The results suggest that mechanical and thermal properties can be improved as well as the response of copolymer electrodes to dopamine, with better reversibility and stability as compared to PCz electrodes. However, the content of carbazole in the copolymer structure is not easy to govern by electrosynthesis. Additionally, water-soluble copolymers of acrylic acid (AA) and acrylamide (AAm) containing low percentages of NVCz have been synthesized previously [19].

In this article, P[NVCz-co-Sty] and P[NVCz-AN] copolymers were prepared by using CAN as an oxidizing agent (in a controlled amount). The polymerization was controlled in a way to obtain a copolymer through the vinyl groups. As a result of this process, white−colored polymers were formed and they dissolved in N,N-Dimethlyformamide (DMF) for chemical oxidation and in Dicholoromethane for electrochemical oxidation, which yields dark green polymers as a result of oxidation of the aromatic rings of the NVCz. Electrochemical film formation of mentioned copolymers on platinum electrode was achieved and the films were characterized.

2. EXPERIMENTAL

2.1 Materials

CAN (Aldrich), NVCz (Aldrich), Styrene (Aldrich), Acrylonitrile (Fluka), tetraethyl ammoniumperchlorate (TEAP) (fluka) (Merck), Dichloromethane (Merck), acetonitrile (Carlo Erba) DMF (Merck) were all highest reagent grade chemicals and were used as obtained.

2.2 Instrumentation

A conventional three-electrode system was used for electrochemical oxidation. The anode and cathode were Pt wire, the reference electrode is Ag wire, and the ferrocene couple has a redox potential, $E = 0.35\,V$, vs this reference electrode. The electrochemical measurements were carried out using WENKING POS 73 potentiostat connected with a Kipp and Zonen X-Y recorder. Fourier transform infrared (FT-IR) spectra were recorded using a Mattson 1000 spectrophotometer by the use of KBr pellet. The electrical conductivity measurements were performed with a Keithley 617 solid-state electrometer.

3. RESULTS AND DISCUSSION

3.1 Polymerization Procedure

The polymerization was carried out in a pyrex vessel (100 ml) at 25°C. The calculated quantity of CAN was dissolved in a known minimum volume of acetonitrile and the solution added to the desired amount of monomer solution in CAN. The mixture was stirred continuously during the polymerization process (20 min). A white powder formed almost instantaneously and then during the reaction time. After filtration, the unreacted monomer was washed away with acetonitrile and the solid was dried in a reduced vacuum.

3.2 Effect of NVCz/St or NVCz/AN Ratio on the Yield

At high CAN, AN and St concentration, the yield decreases, probably due to the effect of termination of both monomers on the copolymerization of NVCz, which at high CAN concentration is known in the literature [17]. It can be seen that AN or St accelerates the reaction to a certain extent, but then decreases the yield of polymerization reaction Table 1 shows the polymerization yield at different [NVCz]/[St] and [NVCz]/[AN] ratios at $[\mathrm{CAN}] = 2.5.10^{-4}$. Yield is calculated by the following equation:

$$\%\ \text{Yield} = [\text{the amount of obtained polymer}/\text{the amount of monomer (NVCz)}] \times 100$$

3.3 Cyclovoltammetric Results

0.0040 g homopolymer of PNVCz and P(NVCz-St), P(NVCz-AN) copolymers were dissolved in 4 ml of CH_2Cl_2, and 0.05 M TEAP was used as supporting electrode. Anode and cathode electrodes were Pt wire.

TABLE 1 %Yield of Copolymers of NVCz-St and NVCz-AN

[NVCz]	[St]	%Yield	[NVCz]	[AN]	%Yield
0.2	–	72	0.2	–	72
0.2	0.05	80	0.2	0.05	75
0.2	0.1	75	0.2	0.1	71
0.2	0.2	77	0.2	0.2	63
0.2	1.0	61	0.2	1.0	55

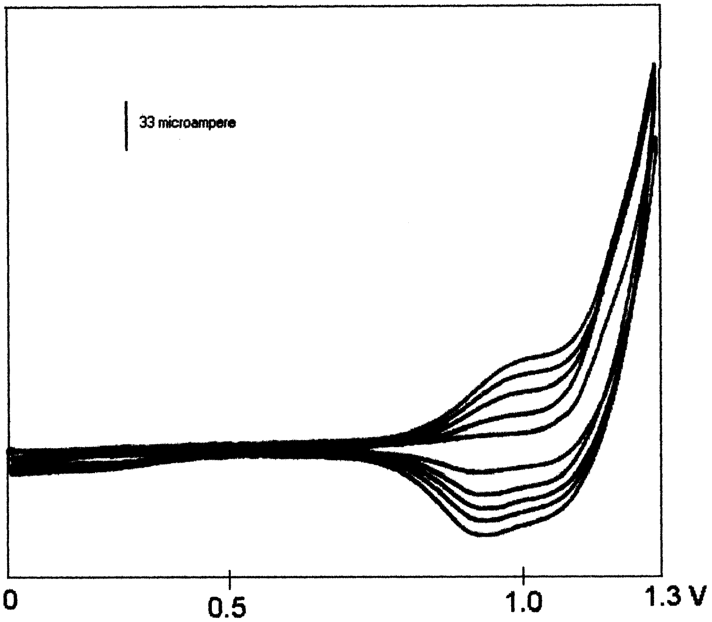


FIGURE 1 CV of PNVCz (scan rate 20 mv/s, 0–1.3 V vs Ag current density 100 μA/cm^2).

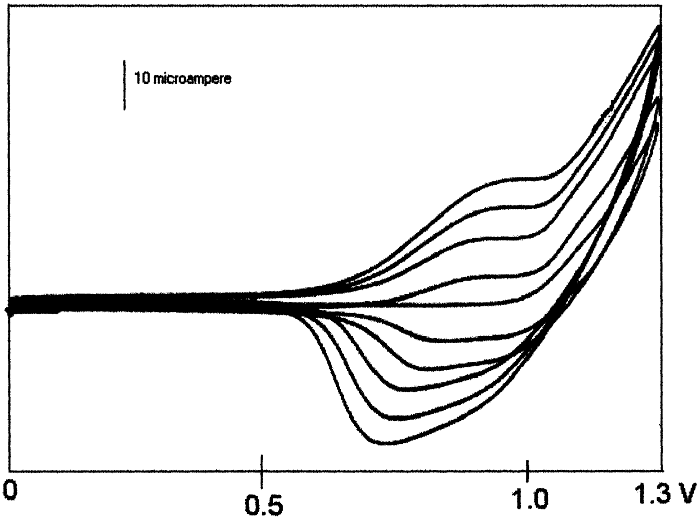


FIGURE 2 CV of P(NVCZ-St) (scan rate 20 mv/s, 0–1.3 V vs Ag current density 54 μA/cm^2).

All polymers were oxidized again by using a single potential scan at 20 mV s^{-1}. Figure 1, Figure 2 and Figure 3 show the cyclic voltammograms corresponding to the potentiodynamic electrooxidation (and electrochemical coating) of PNVCz,P(NVCz-St), and P(NVCz-AN), respectively. Application of potential between 0−1.3 V vs Ag induces the development of a redox system corresponding to the doping/undoping process of the growing film. The current density values were extracted from CVs during the doping and undoping process of the polymeric film. Figure 4 shows the relationship between the scan number and current density of homo and copolymers. It can be seen that the current density of copolymers is lower than the homopolymer of PNVCz, which is due to decrasing conjugation. The current density of P(NVCz-St) is also higher than the P(NVCz-AN)

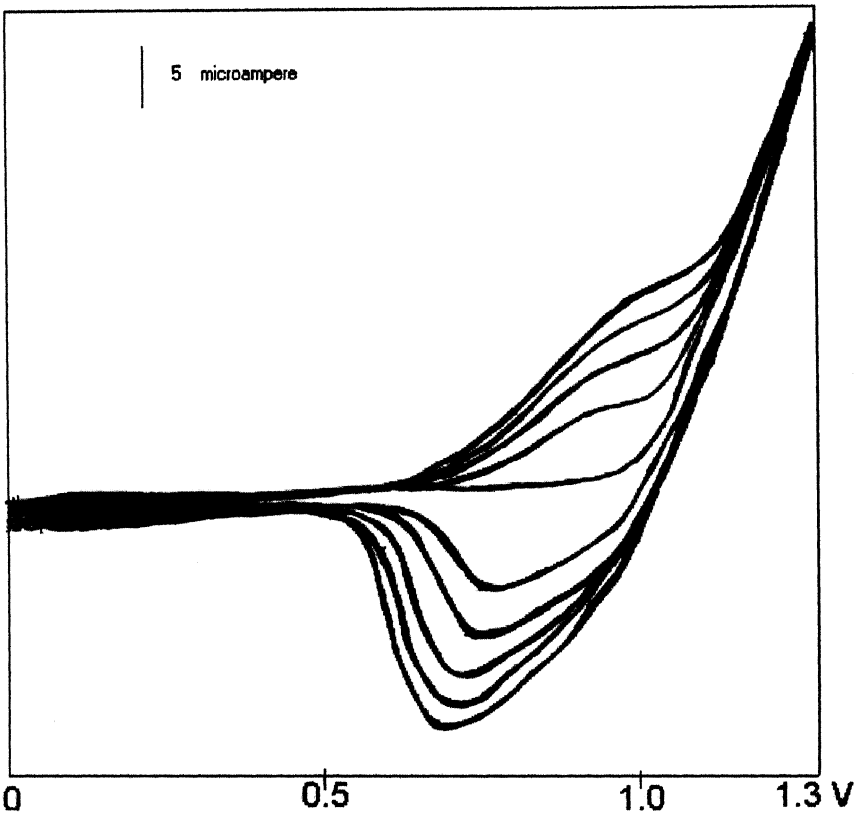


FIGURE 3 CV of P(NVCz-AN) (scan rate 20 mv/s, 0−1.3 V vs Ag current density 18 μA/cm^2).

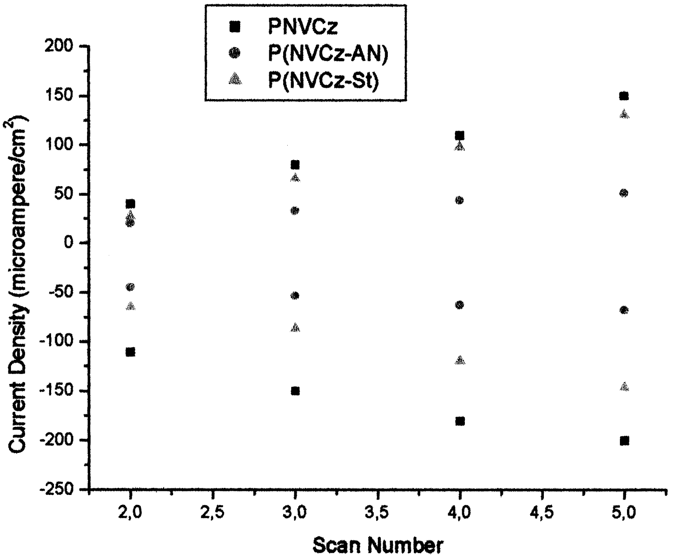


FIGURE 4 Current density-scan number for PNVCz, P(NVCz-St), P(NVCz-AN) (scan rate 20 mv/s, 0–1.3 V vs Ag).

copolymer. This is because of conjugation of the aromatic benzene ring present in the styrene.

3.4 Electrochemical and Chemical Oxidation

0.0040 g/4 ml of homopolymer of PNVCz, P(NVCz-St), P(NVCz-AN) copolymers were dissolved in CH_2Cl_2 and 0.05 M TEAP was used as supporting electrode. Anode and cathode electrodes were stainless steel. A constant potential was applied and a green dark polymer was coated on anode for all polymers. Obtained polymers were lifted off the electrode (free-standing film) for conductivity measurements. For chemical oxidation, previously obtained polymers (0.01 g/10 ml) dissolved in DMF and 0.01 M of CAN was added to the solution until the dark green polymers were obtained. Obtained polymers were prepared as pellet and used for conductivity measurements. Figure 5 and Figure 6 show conductivity, [St]/[NVCz] and [AN]/[NVCz] ratio relationship for electrochemical and chemical oxidation, respectively. It can be seen that with increasing amount of St or AN in the copolymers the conductivity decreases, which is due to decreasing conjugation. Also, oxidized homo polymer of PNVCz has conductivity

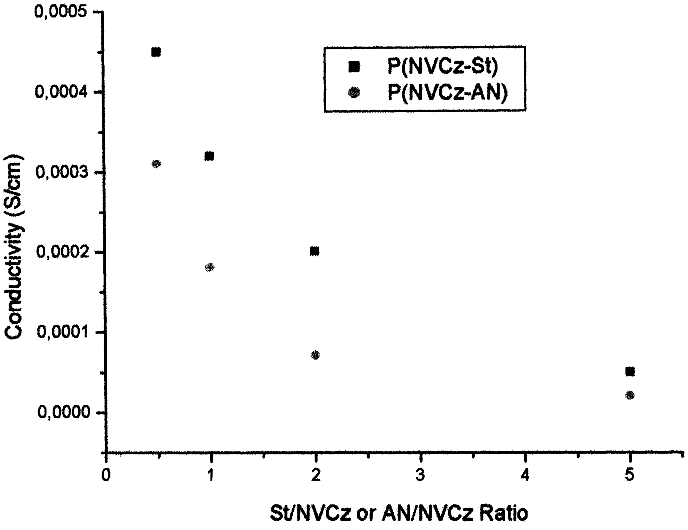


FIGURE 5 ST/NVCz and AN/NVCz ratio-conductivity (obtained by electrochemical oxidation at constant potential).

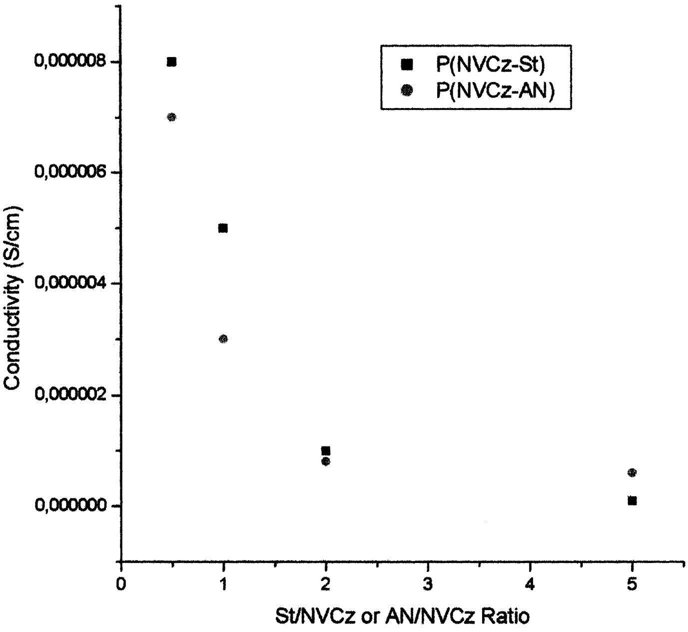


FIGURE 6 ST/NVCz and AN/NVCz ratio-conductivity (obtained by chemical oxidation by 0.01 M CAN).

of 6.10^{-4} S/cm, which is higher than the copolymers. All these results are similar to current density results that were obtained from cyclic voltammetry. The current density is higher for the homopolymer of PNVCz and decreases in the case of P(NVCz-St) and P(NVCz-AN). Here, both obtained results from conductivity and the cyclic voltammetry support each other and also indicate the introduction of vinyl monomer into the structure. Chemical and electrochemical oxidation of the polymers are achieved for characterization and also for obtaining electronically conductive polymers the electrochemical oxidation of the polymers leads to the coating of stainless steel and these copolymer–modified electrodes can be used for biosensor applications. A similar method was used for the coating of stainless steel by NVCz acrylamide copolymers by our group, and the electrochemical response of the copolymer modified electrode to dopamine was successful [20].

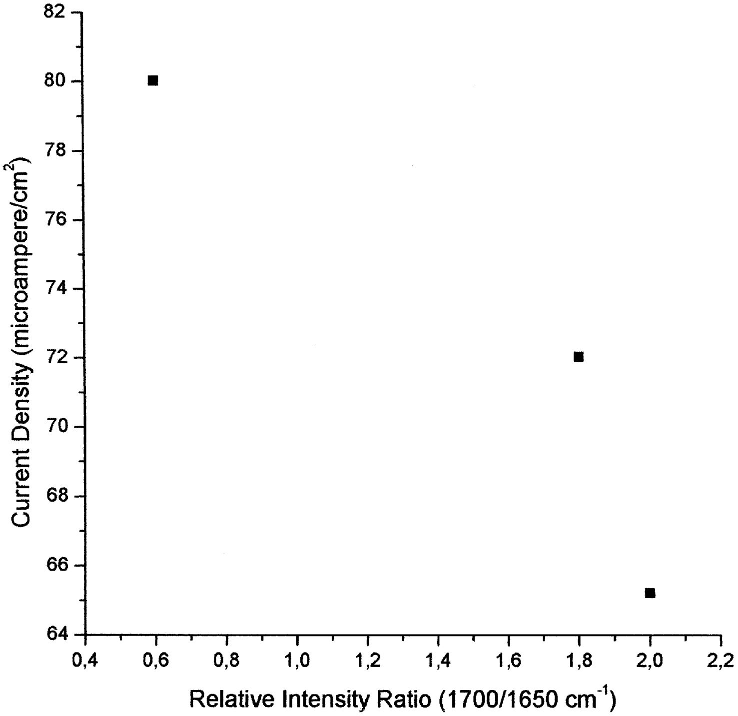


FIGURE 7 Relative intensity ratio of peaks (1700/1650 cm^{-1})—Anodic Current Density at 2. Cycle for St/NVCz = 0 (PNVCz), St/NVCz = 1, St/NVCz = 5.

3.5 FTIR Results

NVCz can be polymerized through the vinyl groups when the monomer concentration is five times greater than oxidant concentration [12]. Under these conditions the resulting polymer (PNVCz) was white. In the FTIR spectrum of white PNVCz, the intensity of vinyl bands at 916 and 850 cm^{-1} decreased compared to the monomer's and there was no decrease in the intensity of C-H out of plane deformation [21]. These results showed that polymerization takes place through vinyl group.

The ratio of % transmission intensity of the peaks in the PNVCz and P(NVCz-St) and P(NVCz-AN) changes with increasing styrene or acrylonitrile in the copolymer. The relative intensity ratio of the 1700/1650 cm^{-1} bands (which corresponds to $-C=C$ streching) is 0.66 for PNVCz. In the case of P(NVCz-St), with changing the amount of

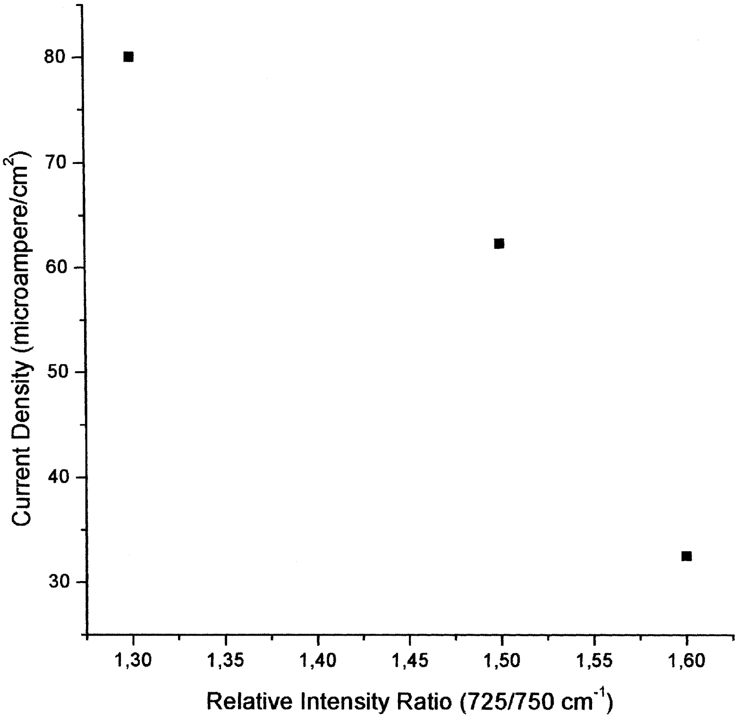


FIGURE 8 Relative intensity ratio of peaks (725/750 cm^{-1})—Anodic Current Density at 2. Cycle for AN/NVCz = 0 (PNVCz), AN/NVCz = 1, AN/NVCz = 5.

styrene during chemical polymerization, the ratio of the peaks becomes 1.8 and 2.0 for St/NVCz = 1, St/NVCz = 5, respectively. In the homopolymer of PNVCz, the relative intensity ratio of 725/750 cm^{-1} bands (C-H out of plane bending) is 1.33. In the case of P(NVCz-AN). With changing amount of acrylonitrile during chemical polymerization the ratio of the peaks changes to 1.5 and 1.6 for [AN]/[NVCz] = 1 [AN]/[NVCz] = 5, respectively. Figure 7 and Figure 8 show current density change of the polymers with changing ratio of the observed

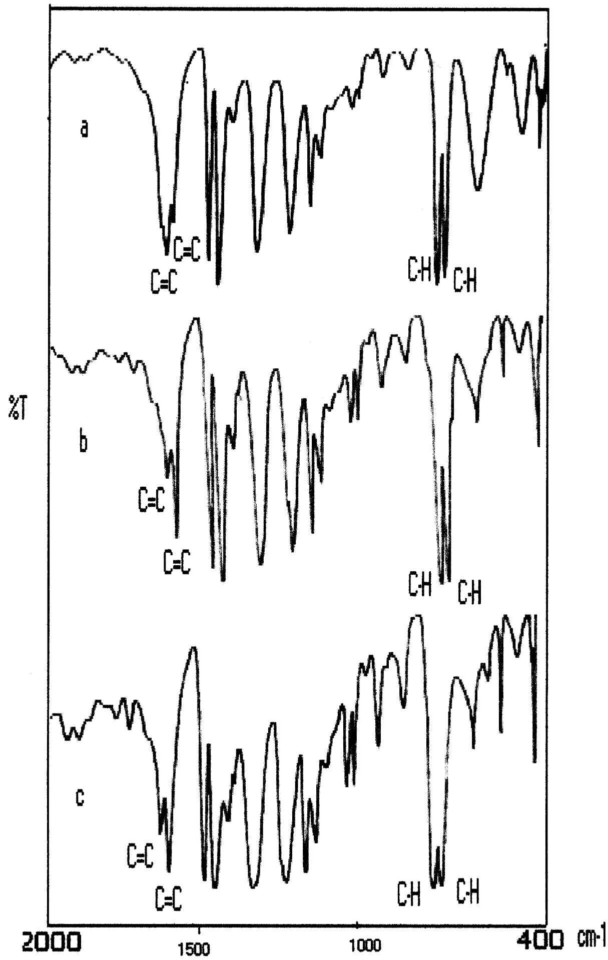
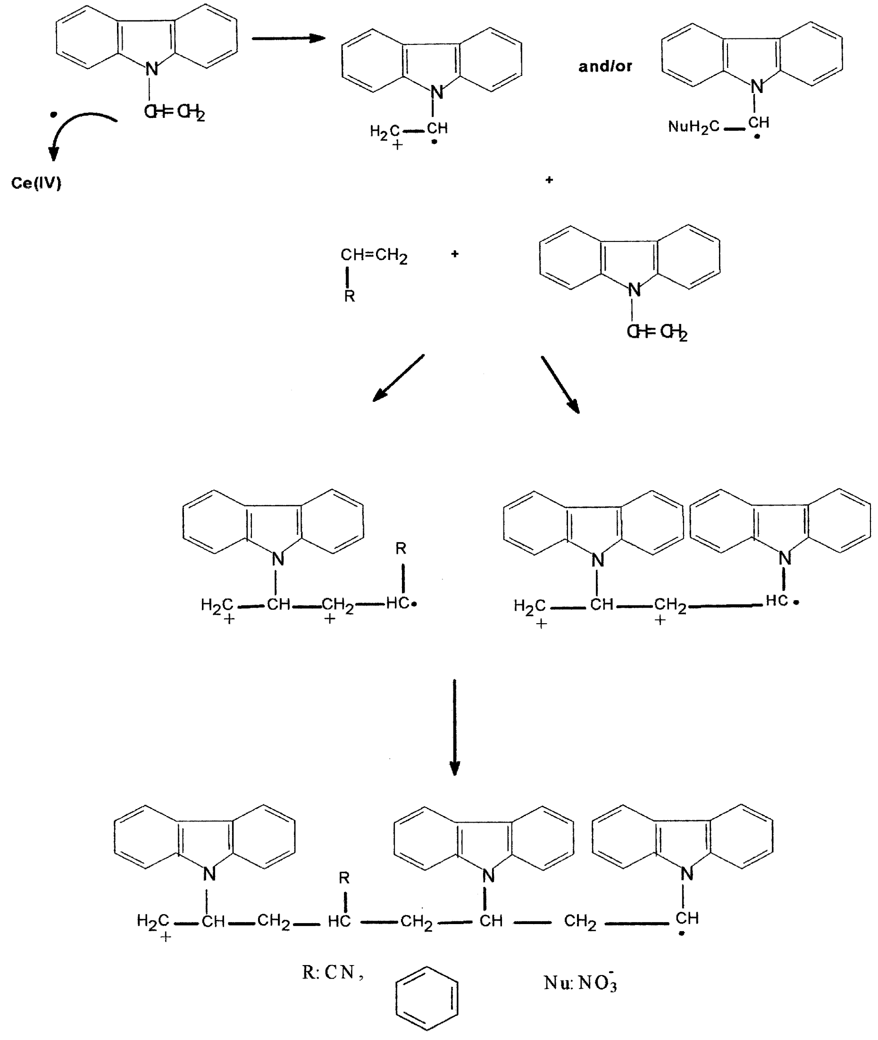


FIGURE 9 FTIR spectrum of a) PNVCz, b) P(NVCz-St) (NVCz/St = 1/5), c) P(NVCz-AN) (NVCz/AN = 1/5) between 2000, 400 cm^{-1}.

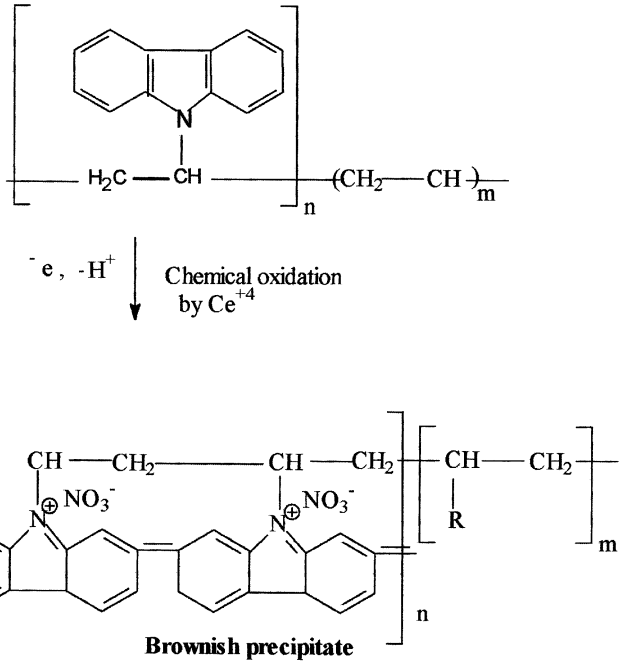
peaks. This is due to increase of [St]/[NVCz] or [AN]/[NVCz], (changing ratio of the peaks observed). The current density decreases because the observed polymers are less conductive compared with the homopolymer of PNVCz. Figure 9 shows the FTIR spectrum of PNVCz,P(NVCz-St) ([NVCz]/[St] = 1/5),P(NVCz-AN)(NVCz/AN = 1/5).

For chemical polymerization, we proposed a similar mechanism with the literature. As has been mentioned, if the oxidant concentration is

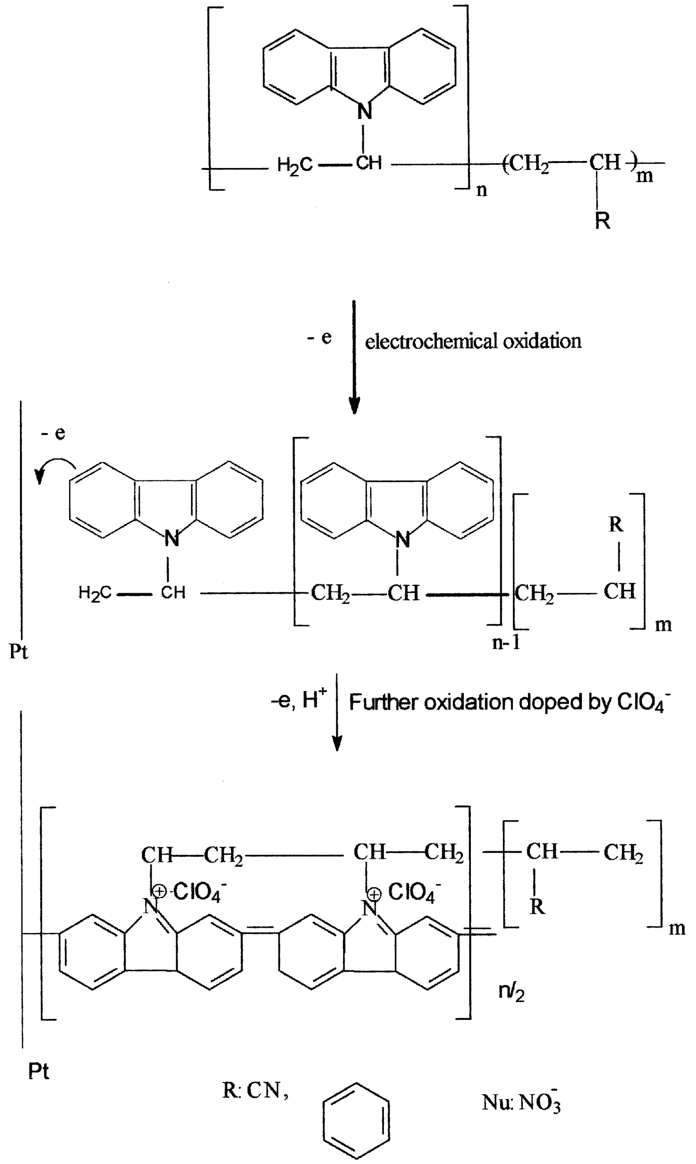


SCHEME 1 Tentative mechanism for chemical polymerization.

five times lower than the monomer concentration a white polymer is formed for NVCz, indicating that polymerization proceeds through the vinyl groups [22]. Also, Tazuke has suggested that the initiation process for the polymerization of NVCz catalyzed by oxidizing metal salts is most likely to be of an electron transfer type [11]. We suggest a mechanism that an electron transfer from NVCz to CAN results in radical cation that can be reacted by a nucleophile (NO_3^-) forming a radical by the addition reaction of this active radical cation or radical with NVCZ or St, AN, and polymerization growth is obtained. Scheme 1 shows the tentavive mechanism proposed for chemical polymerization. For electrochemical and chemical oxidation of this polymer, we suggest a similar mechanism to copolymerization of carbazole-acrylamid (18–23). Electrochemical and chemical oxidation of this polymer mostly takes place from 3-position, which is most reactive. An electron transfer yields a radical cation, and coupling of this radical cation causes the elimination of H^+ and forms a conjugated system which is conductive. Scheme 2 and Scheme 3 show the tentative mechanism proposed for chemical and electrochemical oxidation, respectively.



SCHEME 2 Tentative mechanism for chemical oxidation.



SCHEME 3 Tentative mechanism for electrochemical oxidation.

CONCLUSION

PolyCarbazole and its derivatives have been suggested for a number of applications such as catalyst, photoactive devices, sensors and electrochromic displays (1, 2). However, poor mechanical properties limit the use of these polymers. Coprocessing of these polymers may, therefore, offer some improvements in mechanical properties and processing technology [24,25]. Electrochemical coating random copolymers of P(NVCz-St), P(NVCz-AN), which are obtained by free radical polymerization by Ce(IV), on Pt was probably achieved for the first time for this type of vinyl-conjugated copolymer. The main reason for this was to obtain flexible material compared to NVCz. The presence of both monomers and their electropolymerization gives copolymer of NVCz, probably reacting mainly through the aromatic ring at high potentials and inclusion of vinyl monomer is not realized. This system also gives a better control of pre-copolymer, which can be easily synthesized and its properties can be tailormade before electrocoating. Additionally, the study gives clues about random electro-copolymerization of vinyl-conjugated systems, i.e., controlling feed ratio and other parameters.

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