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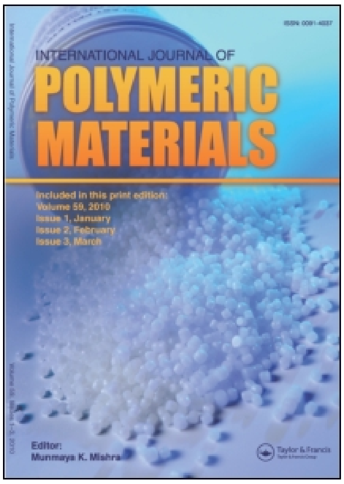

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ELECTROCHEMICAL COPOLYMERIZATION OF N-METHYL PYRROLE WITH CARBAZOLE

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ELECTROCHEMICAL COPOLYMERIZATION OF N-METHYL PYRROLE WITH CARBAZOLE

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Electrocopolymerization of N-methylpyrrole (NMePy) and Carbazole (Cz) was conducted in acetonitrile. Oxidative chemical random copolymerization of NMePy and Cz was also realized by Cerium (IV) ammonium nitrate (CAN) for comparison. The properties of the resulting copolymers were investigated by spectroscopic methods (UV-VIS, FT-IR), cyclic voltammetry and four point probe conductometer, to understand the oligomeric pyrrole ring interaction with carbazole ring where the reactive nitrogen of pyrrole ring was capped (substituted) by methyl group.

Keywords: electrocopolymerization, oxidative copolymerization, N-methylpyrrole, carbazole, UV-VIS, FT-IR, cyclic voltametry, four point probe conductometer

INTRODUCTION

π-Conjugated polymers have been promising advanced material candidates for more than two decades [1]. Carbazole-containing polymers [2], especially those with carbazole as pendant unit or copolymers, have been extensively investigated due to their hole transport ability, photorefractive, and high temperature dielectric properties. The random copolymerization of heterocyclics is of interest because the properties of the resulting conductive polymers can be improved. Electrochemical synthesis permits direct grafting of the conducting polymer onto the electrode surface, which can be of special interest for electrochemical applications. As the electrical potential

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needed for monomer oxidation is significantly higher than the charging (or doping) of the formed polymer, the polymer is directly obtained in its conducting state. The film thickness can be easily controlled by the electrical charge employed during polymerization. Also chemical polymerization by CAN used for comparison is very effective for heterocyclic monomer polymerization [3]. At present, there is much interest in electrically conducting heterocyclic polymers, of which polypyrrole (PPy) is the best known example. PPy is often formed by electropolymerization although there are some reports of polymerization using oxidizing metal salts [3–4]. Attempts have been made in the copolymerization of pyrrole (Py) with other heterocyclic monomers to improve the properties of the resulting product. So far, Py and N-methyl pyrrole [5], Py and phenol [6], Py and terthienyl [7], Py and tetraalkyl ammonium [8], Py and acrylamide [9] have been prepared by electrolytic oxidation of the mixture of monomers. Additionally, there are some studies on the copolymerization of carbazole derivatives with some fumarates and vinyl monomers [10–11]. Although the copolymer of Py and N-vinyl carbazole (NVCz) was obtained electrochemically [12–13] and chemically, copolymerization of N-methyl pyrrole (N-MePy) with carbazole (Cz) is not reported.

Of all known conducting polymers, polypyrrole is the most frequently used in commercial applications, due to the long-term stability of its conductivity and the possibility of forming homopolymers or composites.

In addition to electrochemical polymerization, alternative chemical methods of synthesis are being developed, even for electrochemical applications such as electrodes, batteries, sensors, and so on. This is a consequence of the two main problems associated with the electrochemical polymerization of pyrrole. The first problem is related to the difficulty in producing large amounts of polypyrrole, due to the limitations imposed by the size of the anode. The second problem associated with electrochemical synthesis of polypyrrole seems to be related to the difficulties in characterization of the obtained polymer, and its polymerization mechanism. The simplest study of pyrrole electropolymerization involves different experimental variables in order to optimize polymer properties. These variables can be chemical, (i.e., solvent or reactants, monomer, and dopant salt) or physical (i.e., temperature, nature, and shape of the electrodes, cell geometry, etc.)

The copolymerization of pyrrole (Py) with other heterocyclic monomers was also performed with the aim of improving the properties of the resulting products [9, 14]. In this study, random copolymerizations of NMePy with Cz were performed electrochemically and chemically.

Use of N-methyl substituted pyrrole has the advantage of preventing polymerization through nitrogen, which causes a decrease in conductivity (defect in conjugation of copolymer is prevented).

EXPERIMENTAL

Acetonitrile (ACN), N-Methylpyrrole (N-MePy), and sodium perchlorate ($NaClO_4$) were obtained from Merck, carbazole (Cz) (Aldrich), Cerium (IV) ammonium nitrate (Carlo Erba) (CAN), 0, 1 M $NaClO_4$ in acetonitrile (ACN) as an electrolyte, and all chemicals were used as supplied. Electrochemical polymerization was carried out in the range of 0−1.1 V. A three electrode system was used for cyclo-voltammetric measurements; a Pt plate as the working electrode ($0.03\,cm^2$), a Pt spiral for the counter electrode, and a Ag wire reference electrode in acetonitrile containing 0.1 M Tetrabutylammoniumperchlorate (TBAP) were used. All measurements was taken at 20°C. A Wenking POS 73 model scanning potentiostat connected with a Kipp and Zonen X-Y recorder was employed for electrochemical polymerization.

Fourier transform infrared spectroscopy (FTIR) spectra of polymers and copolymers were taken on a Matson 1000 FTIR spectrophotometer in KBr pellets, in the range of 4000 to $400\,cm^{-1}$.

UV-VIS spectra of polymer films were obtained by using a Shimadzu 160 A Recording Spectrophotometer.

The solid state electrical conductivity measurements—by four-point-probe method—were performed on the prepared pellets of copolymer obtained by oxidative chemical polymerization, or films removed from electrode surface in the case electrochemically synthesized copolymers. These measurements were performed by a Keithley 617 electrometer connected to a four-probe head with gold tips, and electrical conductivity was calculated from the following equation

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

where dn is thickness in cm, V is applied potential in volts, and I is current in amperes.

RESULTS AND DISCUSSION

In order to understand the structure and copolymerization reaction, different mole ratios of N-methyl pyrrole-carbazole (N-MePy/Cz) were

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used for copolymerization and the products characterized by different methods. Cerium (IV) ammonium nitrate (CAN) is used frequently in pyrrole polymerization because of its clean stoichiometry and strong oxidizing power [15].

The Effect of the Amount of CAN on the Copolymerization Yield

%Copolymerization yield = [weight of copolymer (g)/weight of comonomers(g)]. Table 1 indicates that when the amount of CAN increases, polymerization yield increases.

FT-IR Results

Py, MePy, and Cz, were polymerized and copolymerized chemically with CAN. Their IR Spectra are shown in Figure 1. The FT-IR bands of homo and copolymers are assigned in Table 2. FTIR of Poly[NMePy-co-Cz] has a different characteristic spectrum than that of homopolymers [Fig. 1]. The peak at 3424 cm^{-1} of FTIR spectrum of PCz is shifted 40 cm^{-1} in the FTIR spectrum of poly[NmePy-co-Cz]. The peak at 1333 cm^{-1} in the FTIR spectrum poly[NMePy-co-Cz] showed the incorporation of Cz. The new bands at 1433 and 1333 cm^{-1} appeared in the FTIR of poly[NMePy-co-Cz] unlike the homopolymers. Importantly, the intensity of the peak at 1600 cm^{-1} strongly decreased and gave only a small shoulder in the copolymer spectrum.

Because the amount of Cerium in the polymeric structure would be expected to be very little, and due to the difficulty of determination of it the authors have developed a following route by using FTIR spectrum of polymer by using peak corresponding to Cerium or ligands of CAN (namely N—O groups). The poly[NMePy-co-Cz] obtained in different CAN concentrations, and FTIR spectra of obtained copolymers were

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TABLE 1 The Effect of the Amount of CAN on the Copolymerization Yield [MePy] = 0.06 M, [Cz] = 0.06 M

[CAN]*10^2, mol.dm^{-3}	%Yield
0.5	9.60
1.0	12.20
2.0	16.80
3.0	21.24
4.0	24.38
5.0	34.72

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TABLE 2 Some Characteristic FT-IR Bands Assignments of Chemically Prepared Homopolymers and Copolymers

PMePy cm^{-1}	PCz cm^{-1}	PMePy/Cz cm^{-1}	Assignment of peaks
—	3424	3464	N—H str
2900	—	3050–2933	Aliphatic C—H
1600	1605	1600	—N—H Bending
1433	1456	1433	Aromatic —C=C str
1383	1380	1383	—N—O str. Of NO_3^- group
—	1326	1333	Aromatic N—C
—	1236	—	C—H in plane deformation of aromatic ring
1100–1083	1055	–1100	C—H vibration of trisubstituted aromatic
925	—	925	1,3,4 trisubstituted pyrrole (spr)
—	880	874	1,2,4 trisubstituted benzene (sbr)

taken. To understand the effect of CAN concentration and inclusion of Cerium into resulting polymer from the results of FTIR, a graph was plotted of CAN concentration versus %FTIR transmission [intensity of CAN(N—O)peak/intensity ArC-H(due to Carbazole)peak]. As CAN content increases the intensity of Cerium(or CAN) peak increases [Fig. 2].

There is no chemical study to find the amount of CAN in the copolymer because the amount of obtained copolymer is very little.

UV-Visible Spectrophotometric Results

Ex-situ spectrophotometric measurements were carried out to characterize poly[N-MePy-co-Cz] obtained by chemical polymerization. In the case of PPy the maximum absorbtion peaks are 821, 438, 365 nm. The maximum absorbtion peaks of PCz at 725, 400, and 322 nm [16] arise from the bonding level to antibonding level to π^* conduction band. In the case of poly[N-MePy-co-Cz] are at 971 and 48 nm. These maximum absorbtion peaks are unlikely to appear in the homopolymers.

Polyaromatics such as polypyrrole, poly(phenylene), polythiophene have nondegenerate ground state and two limiting mesomeric structures, that is, aromatic and quinoidal are not energetically equivalent, the quinodial having higher energy [17]. In these problems the removal of an electron from the conjugated system provokes a local distortion of the chain and appearance of two states in the gap corresponding to a polaron (or radical cation) with spin of 1/2. Theoretical

TABLE 3 UV-Visible Spectra of Co-Oligomers in the Range of Wavelengths of 484–971 nm, by Changing [Ce(IV)] at Constant MePy and Cz Concentrations

$[Ce(IV)]_0$, M $\times 10^2$	Abs (971 nm) $\times 10^3$	Abs (484 nm) $\times 10^2$
0.05	122	19
0.5	192	99
2	312	103
3	473	131
5	484	135

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calculations have shown that adjacent polarons are unstable and lead to the formation of spinless doubly charged defects, for example, bipolarons (or dications), which have been proposed as the dominant charge storage species [17]. Similarly, in this study the authors take UV-Visible spectrum of the soluble portions of oligomers observed in solution after precipitating the polymer. The authors investigated, what will change in the UV-visible spectrum while the amount of oxidant increases. In the spectrum, the peaks at 971 and 484 nm are observed when it is oxidized. Table 3 shows that the peak at 484 nm might indicate that further oxidation of the conjugated system results in a radical cation that indicates the polaron [15], and the peak at larger wavelength (971 nm) corresponds to bipolarons [15] (dication-further oxidized). As the initial amount (feed ratio) of CAN increases, the absorbances of these two peaks increases (Table 3). UV-VIS spectrophotometric results indicate the produced soluble N-MePy-co-Cz oligomers increase in solution by increasing the concentration of initiator (CAN).

Conductivity Characteristics

Conductivity of Copolymers Obtained by Oxidative Chemical Polymerization

Increase in CAN concentration at constant $[NMePy]_0/[Cz]_0$ ratio of 1 gives almost a linear increase in conductivity of the resulting copolymer which is also indicative that increase in CAN concentration (corresponding to the increase in oxidation potential-or ability) results in a longer chain of copolymer (longer conjugation and more polaron and bipolaron structure formation) and/or inclusion of cerium into the copolymeric structure [Fig. 3]. In addition to both possibilities, the latter seems to be more probable for this case because the corresponding cerium (and/or related nitrate ligands) peaks strongly appeared at about 1380 cm^{-1}.

Conductivity of Copolymers Obtained by Electrochemical Polymerization-Comparison with Soluble Oligomer Concentrations

In electrochemical polymerization, polymers seem to have more orderly structure than chemical polymerization and, as a result, conjugation of bonds increases, so the conductivity would be higher than in chemical polymerization [15]. In the literature, the polymerization of 3-alkyl thiophenes using $FeCl_3$ as oxidant acquired a growing importance [18–19]. However, it became rapidly evident that polymers produced by this method contained a significant amount of regiochemical defects. Any defect in ideal head to tail relative placement of consecutive monomer units induces a severe steric repulsion between substituents and a distortion of the conjugated chain with a loss of effective conjugation.

This was indeed the case and chemical polymerization conductivity results were lower than electrochemical ones. On the other hand, because the high oxidation potential of CAN is high enough to cause overoxidation, the copolymeric structure after polymerization has more defective structure resulting in less conjugation and conductivity [15].

The conductivity of copolymer film obtained by electrochemical method was measured with the four-point-probe method, while the rest of the solution was analyzed with UV-Visible spectrophotometer for different monomer feed ratios (Table 4). Table 4 indicates that the amount of absorbance at 430 nm decreases and gives a minimum (lowest oligomer amount) for the monomer feed ratio of $[MePy]_0/[Cz]_0$ of 1/3, the resulting copolymer film gives a maximum conductivity. So this explains the fact that when Cz concentration increases up to a certain concentration, the chain length of polymer and the polaron, bipolaron structure, and conjugation increases, which is reflected in

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TABLE 4 Ex-situ UV-Visible Analysis of Soluble Poly[NMePy-co-Cz] or Oligomer and Four-Point Probe Conductivity Measurement of Poly[NMe-Py-co-Cz] while the Amount of Cz Increases

$[MePy]_0/[Cz]_0$	Absorbances at 430 nm. Oligomeric soluble species (polaron)	Conductivity*, (S/cm) × 10^5 of copolymer
1/1	1.0	4
1/2	0.5	6
1/3	0.1	9
1/4	0.3	5
1/5	0.4	3.5

*There conductivities are measured after obtaining free-standing film on stainless steel electrode in two electrode system in 0.1 M $NaClO_4$ in ACN.

the conductivity values. UV-vis spectrophotometric measurements of oligomeric species formed for different comonomer feed ratios, also support this idea.

The amount of oligomer absorbances (the concentrations), that is, at $[\text{N-MePy}]_0/[\text{Cz}]_0$ ratio of 1/3 gives a minimum, [the amount of oligomer (and corresponding polaron structures) decreases], and the solid state conductivity of the corresponding polymers decreases [as a result of Ex-situ measurements] (Table 4).

Electrochemical Polymerization

Cyclic Voltammetric Electrochemical Growth of Copolymer

Carbazole and Py are oxidized at 1.2 v [14], 0.6 v [9] vs. SCE, respectively. In this study, poly[N-MePy-co-Cz], PolyN-MePy, and PCz were obtained electrochemically in $NaClO_4$ electrolyte solution in ACN on Pt electrode. Table 5 indicated that from PMePy to PCz $E_{1/2}$ and ΔE values differentiate, showing that the copolymer is formed, and in variable ratios of monomers showed different electrochemical parameters that is, at 1:1 ratio of monomers, the polymer film showed reversible behavior.

Figure 4 shows the current densities of peaks (shown in Figure 5) obtained during electrogrowth of copolymer on electrode surface by electrochemical means (against cycle-scan-numbers). The current densities of peaks obtained from the copolymers are greater than that of PCz.

Figure 4 indicates that peak currents vs. scan numbers (which is proportional with electrical charge) increase linearly, therefore increase in charge (Q) results in a formation of more radical ions ($R^{+\bullet}$), so chain length of copolymer increases and as a result the conductivity increases (Table 4). Slope of lines of current vs. scan rate

TABLE 5 Some Electrochemical Values Obtained from Polymer Growth of Homopolymers and Copolymers [WE = Pt, CE = Pt, RE = Ag wire]

	$E_{ox,m}$	E_a	E_c	$E_{1/2}$	ΔE
PMePy	0.84	0.45	0.34	0.395	0.11
P(MePy-co-Cz) 1:1 monomer ratio(MePy/Cz)	1.1	0.56	0.52	0.54	0.04
P(MePy-co-Cz) 1:2 monomer ratio(MePy/Cz)	0.87	0.45	0.23	0.34	0.22
P(MePy-co-Cz) 1:3 monomer ratio(MePy/Cz)	1.01	0.37	0.18	0.28	0.19
P(MePy-co-Cz) 1:4 monomer ratio(MePy/Cz)	0.94	0.38	0.28	0.33	0.10
PCz	1.2	0.7	0.66	0.53	0.04

*Potentials were measured in volt.

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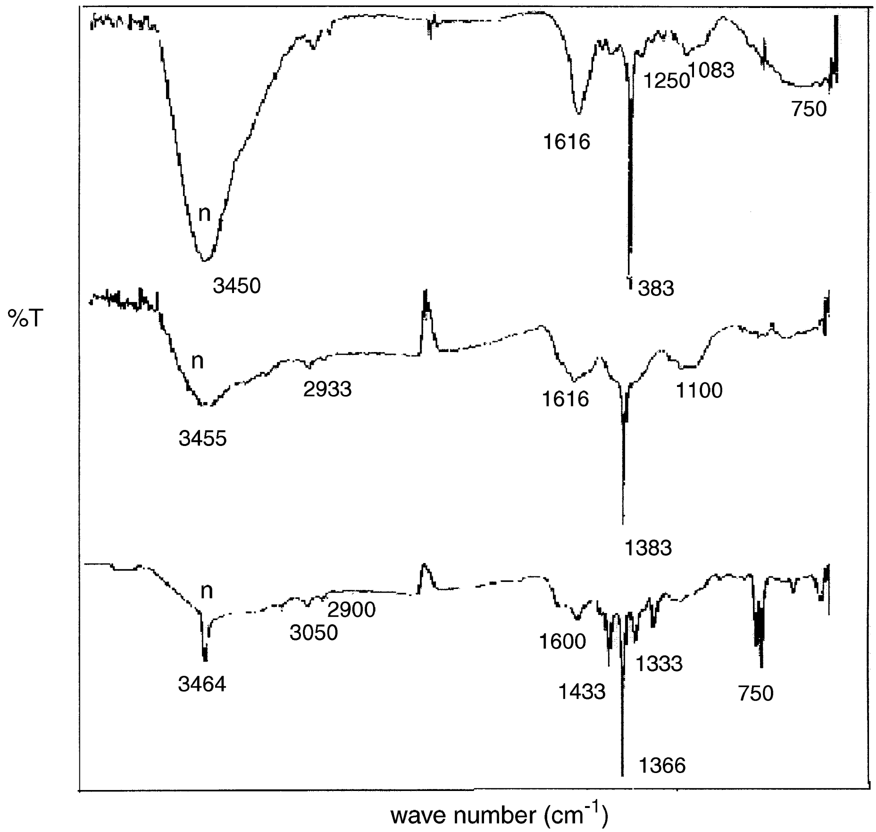

FIGURE 1 FT-IR spectra of a) PCz; [Cz]$_0$ = 0,12 M, [CAN]$_0$ = 0,06 M b) PMePy; [NMePy]$_0$ = 0.06 M, [CAN]$_0$ = 0.06 M, c) Poly[NMePy-co-Cz], [NMePy]$_0$ = 0.06 M, [Cz]$_0$ = 0.06 M, [CAN]$_0$ = 0.02 M.

(or charge) of copolymer seems to be additive slope of corresponding monomers (slope of NMePy + Slope Cz = slope of Cz-NMePy). As a result, it may be assumed that, in the presence of Cz and MePy, a new structure (copolymer) is formed and it seems that this method (CV) can be used for such evaluations.

The poly[N-MePy-co-Cz] is obtained electrochemically in 0.1 M NaClO$_4$ electrolyte on Pt electrode (0.03 cm^2). In different [NMePy]/[Cz] feed ratios, the copolymers are obtained by using CV (CV is taken in three electrode system). Cyclic voltammograms of copolymers and homopolymers are seen in Figure 5: higher current densities were obtained for the [NMePy]$_0$/[Cz]$_0$ = 1/2 and 1/3 ratios than for [NMePy]$_0$/[Cz]$_0$ = 1/1 ratios. Table 4 shows that the conductivity of

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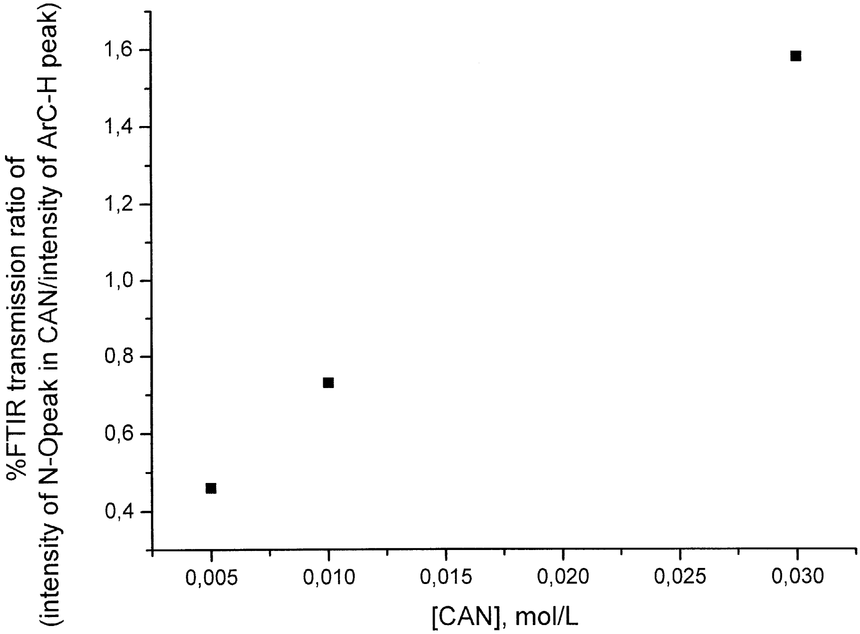

FIGURE 2 The effect of [CAN] on % FTIR transmission (intensity of CAN peak/intensity of ArC-H peak).

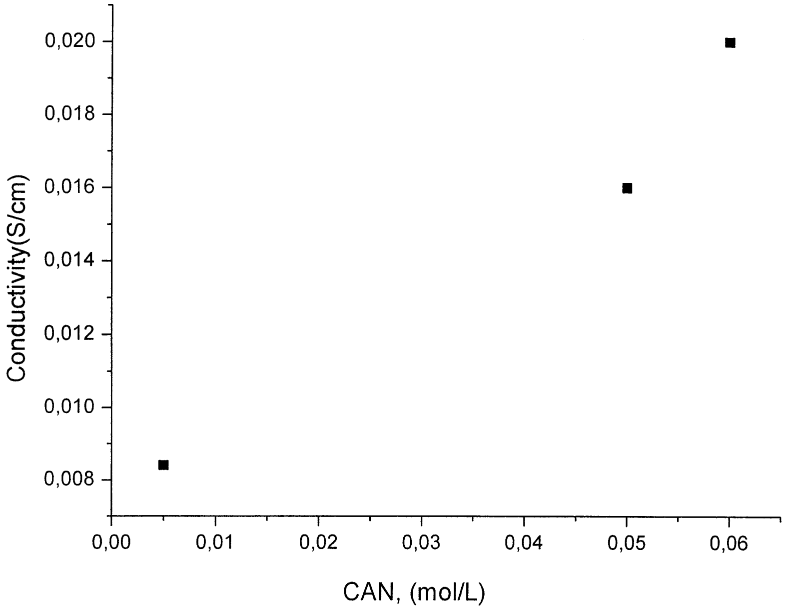

FIGURE 3 The effect of [CAN] on conductivity of copolymer measured by four-point probe technique.

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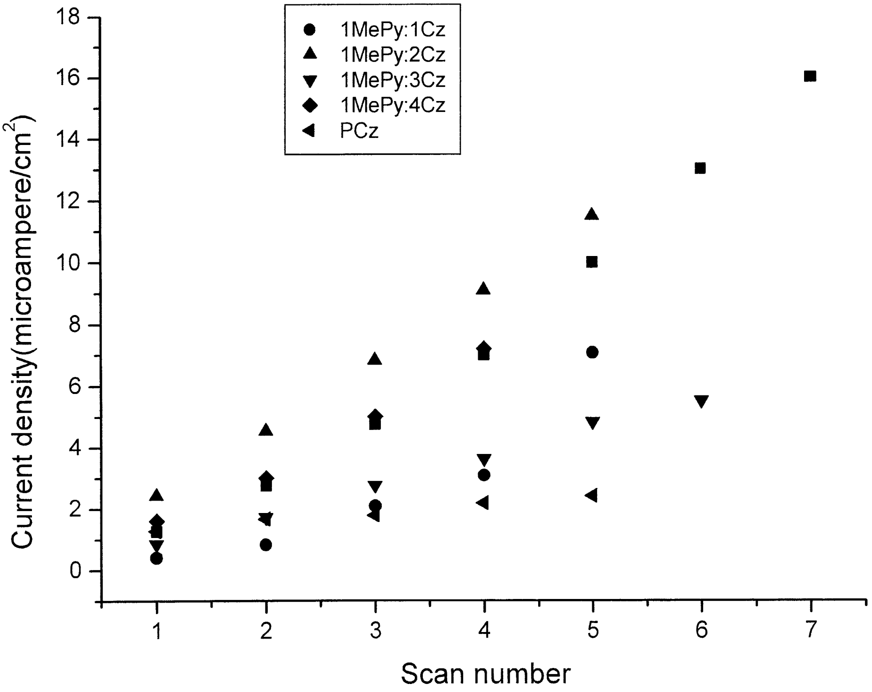

FIGURE 4 Electrochemically formed NMePy, Cz, Cz/NMePy copolymer: graph of current values of cyclic voltamograms versus scan number.

copolymer obtained with $[\mathrm{NMePy}]_0/[\mathrm{Cz}]_0 = 1/2$ and 1/3 ratios is greater than $[\mathrm{NMePy}]_0/[\mathrm{Cz}]_0 = 1/1$; however, that increase did not continue for $[\mathrm{NMePy}]_0/[\mathrm{Cz}]_0 = 1/4$, 1/5 ratio. (Conductivity measurements were done with the copolymer coated on Stainless Steel electrode (SS) in a two electrode system). The graph (Figure 6) is plotted to compare conductivity and current density results, but at these two methods are not at exactly comparable conditions.

According to this plot (Figure 6), for copolymer obtained with $[\mathrm{NMePy}]_0/[\mathrm{Cz}]_0 = 1/2$, the conductivity and current density (obtained from electrogrowth CV of copolymer) increase with Cz concentration. The copolymers, with $[\mathrm{NMePy}]_0/[\mathrm{Cz}]_0 = 1/3$ and 1/4 ratios, deviate from one another. Because the methods and time of electrolysis obtaining the copolymers are different, this comparison is suspect.

CONCLUSIONS

Comparative study of the chemical and electrochemical polymerization of Poly[N-MePy-co-Cz] was performed in this study. These

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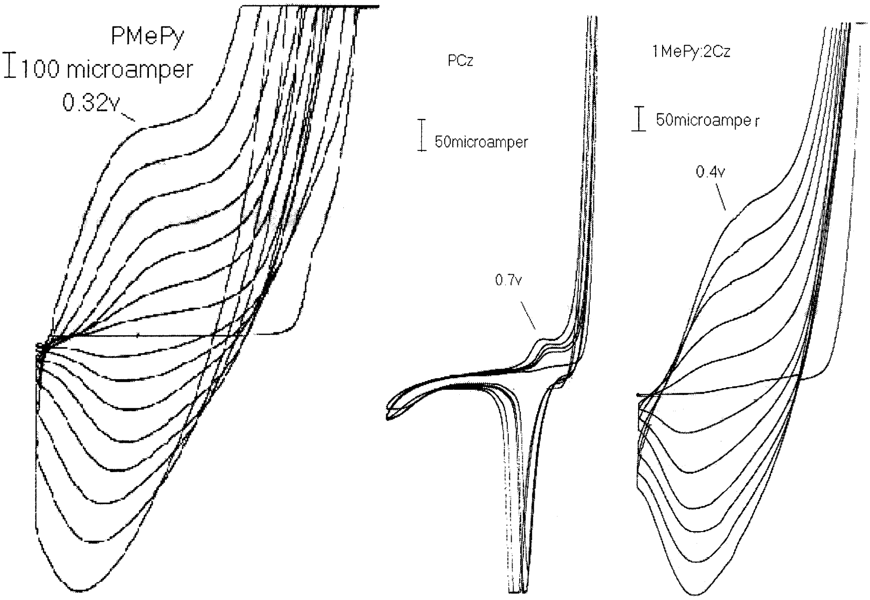

FIGURE 5 Cyclic voltamogram of polymer growth of homopolymers and poly (NMePy-co-Cz).

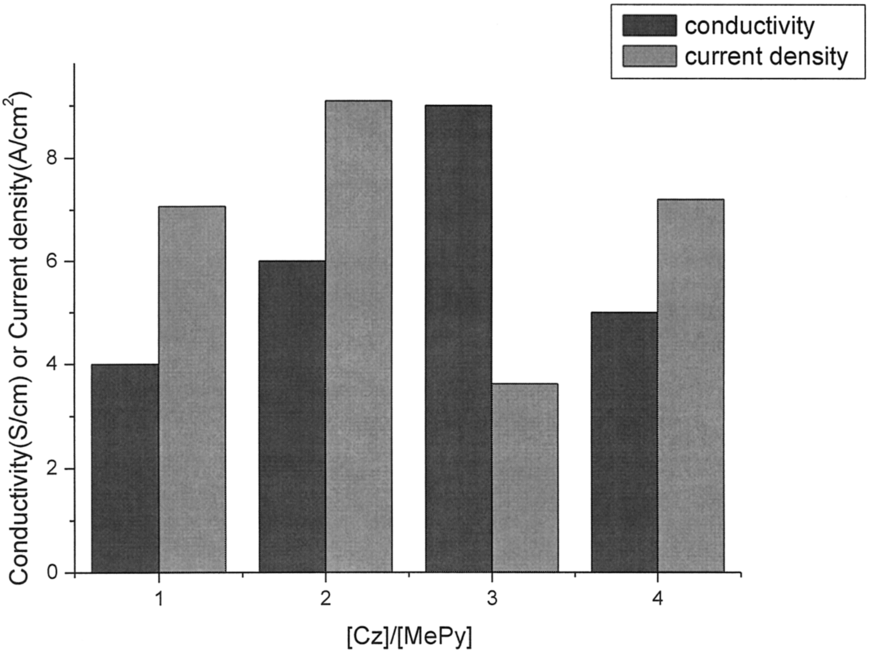

FIGURE 6 Effect of [Cz]/[N-MePy] on conductivity and current density.

methods resemble each other, and they both initiate the polymers by electron transfer reaction either to electrode or Ce(IV).

The properties of resulting copolymers obtained by both routes, were investigated by spectroscopic methods (UV-VIS, FT-IR), cyclic voltammetry and four-point-probe conductometer, to understand the oligomeric pyrrole ring interaction with carbazole ring where the reactive nitrogen of pyrrole ring was capped by methyl group.

In the oxidative chemical polymerization, increase in Ce(IV) concentration resulted in an increase in yield, which has practical advantages.

FTIR spectra of Poly[NMePy-co-Cz], and homopolymers, PNMePy and PCz, indicate a copolymer formation, which has new bands and some shifts in the peaks with respect to homopolymers.

In ex-situ studies of CAN increases, UV absorbance at 484 nm for dimer or trimer (and corresponding polaron structure) increases gradually, and absorbance at 971 nm for larger oligomers (and corresponding bipolaron structure) sharply increases. UV-vis spectrum of poly(MePy-co-Cz) indicated that there are some shifts in the peak potentials compared with homopolymers. This is also supportive information about copolymer formation.

A mechanism of copolymerization can be suggested, as that radical cation formed by oxidative chemical or electrochemical methods, followed by coupling reactions of radical cations or oligomeric radical cations, depending on the ease of oxidation of heterocyclic monomer.

The conductivity of Poly[N-MePy-co-Cz] obtained via CAN is increased with the amount of oxidant, with the possibility of inclusion of Cerium salt as a dopant into the resulting copolymeric structure. Cyclic voltamogram of poly[N-MePy-co-Cz] is different than homopolymers and the current density of all copolymers obtained is higher than polycarbazole.

Ex-Situ UV-vis spectrum of poly[N-MePy-co-Cz] and conductivity measurements of poly[N-MePy-co-Cz] showed that when the amount of Cz increases up to two and three times greater than N-MePy, the polymer chain length increases, and oligomers or soluble polymers in solution decrease. When Cz concentration is higher than this value the condition is reversed.

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