Comparative Study of Chemical and Electrochemical Copolymerization of N-Methylpyrrole with N-Ethylcarbazole Spectroscopic and Cyclic Voltammetric Analysis

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The copolymerization of N-Methylpyrrole (N-MPy) and N-ethylcarbazole (ECz) by chemical and electrochemical methods is investigated in detail. Random copolymers of poly[N-Methylpyrrole-N-ethylcarbazole], P[N-MPy-co-ECz], were synthesized in the presence of ceric ammonium nitrate (CAN) in acetonitrile. Electrocopolymerization of N-MPy, and ECz was carried out in various solvents on platinum electrode. Propylene carbonate (PC) was found to be the most suitable solvent for film formation. The effects of sweep rate, supporting electrolyte type, mole ratio, and temperature on the electropolymerization were discussed. The electrochemical properties of Poly(N-ethylcarbazole), (PECz) were improved on copolymerizing it with N-MPy. A copolymerization mechanism has been suggested. The resulting copolymer was characterized by UV-Vis and FT-IR spectroscopic methods, as well as cyclic voltammetric measurements.

INTRODUCTION

The random copolymerization of heteroatomics has been of interest because the properties of the resulting copolymer can be improved and copolymers obtained by this method would be economically more feasible than the corresponding polymerization of related comonomers

883

(where synthesis is a tedious and expensive process). Among the methods that have been used, oxidative chemical copolymerization [1–4] and electrochemical copolymerization are used to prepare conducting polymers. Research has been expanded on the studies of heteroatomic conducting polymers [5–6], as they have better chemical stability and due to interest in the polaron and bipolaron conduction mechanism [7].

There is much current 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 mentioning polymerization processes using metal salts [8–9]. Attempts have been made in copolymerization of pyrrole (Py) with other heterocyclic monomers to improve the properties of the resulting product. So far, Py and N-MPy [10] Py and phenol [11], Py and terthienyl [12], Py and tetraalkyl ammonium [13] and Py and acrylamide [14] have been prepared by electrolytic oxidation of monomer mixtures. Additionally, there have been some studies about copolymerization of carbazole derivatives with some fumarates and vinyl monomers [15–18]. Notwithstanding the reported attempts to obtain Py and N-vinylcarbazole (NVCz) copolymer through electrochemical processes [19–20] and chemical copolymerization of N-MPy with carbazole (Cz) [21], chemical and electrochemical copolymerization of P[N-MPy-co-ECz] have not been reported yet.

In a previous study of oxidative chemical polymerization by ceric ammonium nitrate (CAN), the results showed that the reaction proceeds through different routes depending on the ceric ammonium nitrate concentration [22]. Among all known conducting polymers, polypyrrole is the most frequently used one, due to its conductivity and the possibility of forming homopolymer, copolymer, or composites with optimal properties. However, it is hard and brittle and these poor properties greatly restrict its potential applications [23–24]. Attempts have been made to obtain composite formation with different polymer matrices [25] and copolymerization of pyrrole (Py) with other heterocyclic monomers in order to improve the properties of the resulting product [26–27]. So far, copolymers of pyrrole with heterocyclic monomers have been prepared by electrolytic oxidation [28–30]. The choice of such monomers (i.e., pyrrole, N-vinylcarbazole, etc.) was not made randomly because the oxidation potentials of these monomers are comparable and the electrochemical oxidation of mixed monomers have successfully produced the copolymer. Conducting polymers and composite films of N-substituted carbazole with pyrrole were prepared electrochemically. It has been found that homopolymer, copolymer, and composite electrodes of N-substituted carbazoles with

pyrrole seem to be stable and sufficiently electroactive for applications employing potential differences (i.e., sensors of different usages).

Carbazole is a prototypical organic molecule that has shown potential for technological applications. Polymers based on this molecule display good electro- and photoactive properties because of their high hole transporting mobility and strong absorption capacity in the UV spectral region. Formation of this polymer is of interest to understand charge transport, because it is highly Π- conjugated compared with other known polymers [31–32]. At the same time, polycarbazole (PCz) derivatives have sparked attention in the study of polymer-modified electrodes [33]. The ability of these polymers to form coherent films depends greatly on the nature of the substituents. It has been found that some substituents such as N-ethyl and N-phenyl do not allow film formation in acetonitrile, although film formation is possible in $HClO_4$ [34]. The synthesis and modification of carbazole-based polymers to obtain polymers exhibiting outstanding and interesting thermal, electrical, photoelectrical, ion exchange, and other physicochemical properties have been reviewed [35]. However, PCz has poor processing properties [36] that need to be improved to suit practical applications.

In the authors' previous comparative study, polymerization of N-MPy in the presence of Cz has been studied by chemical and electrochemical methods [21]. Anticipating the expected additional combined properties of alkyl-substituted pyrrole and carbazole monomers, these have been copolymerized by using N-MPy and ECz monomers. The electrocopolymerization system is investigated in this study at different ratios of the corresponding monomers.

Electrocoating was performed onto Pt from acetonitrile solution of monomers and sodium perchlorate ($NaClO_4$) was used as the supporting electrolyte. Results suggest that the mechanical properties can be improved.

EXPERIMENTAL

Materials

N-methylpyrrole (N-MPy), sodium perchlorate ($NaClO_4$), lithium perchlorate ($LiClO_4$), tetrabutylammonium perchlorate (TBAP), dimethylformamide (DMF), tetrabutylammonium tetrafluoroborate ($TBABF_4$), propylene carbonate (PC), acetonitrile (ACN), and acetone were obtained from Merck. Ceric ammonium nitrate (CAN) was supplied by Carlo Erba, and N-ethylcarbazole (ECz) by Aldrich. These were all high-grade reagents and were used as received.

Instrumentation

The conventional three-electrode system was used for electrochemical oxidation. The anode was a Pt plate as the working electrode ($0.08\,cm^2$), and the cathode was a Pt spiral for the counter electrode, and the reference electrode was an Ag wire. The ferrocene couple had a redox potential, $E = 0.35\,V$, versus reference electrode. The electrochemical measurements were carried out using Parstat 2263 potentiostat, which is a self-contained unit that combines potentiostatic circuit with phase-sensitive detection.

Fourier transform Infrared spectra (FT-IR) of polymers in KBr pellets were taken on a Matson 1000 FT-IR spectrophotometer.

UV-Vis spectra of polymer solutions were performed by using a Shimadzu 160 A recording spectrophotometer.

Chemical Polymerization Procedure

The polymerization was carried out in a pyrex beaker (100 ml) at $25°C$. The measured quantity of CAN was dissolved in a known minimum volume of acetonitrile and the solution added to the required amount of monomer solution in CAN. The mixture was stirred continuously during the polymerization process (20 min). A black precipitate formed almost instantaneously. After filtration, unreacted monomer was washed away with acetonitrile and the residual solid was dried in vacuum.

Cyclovoltammetric Characterization

Electrochemical polymerization was carried out in the range of $0–1.2\,V$ by using cyclic voltammogram. The oxidation potential of monomers on the precoated polymer layer was slightly different from the oxidation potential on bare Pt, as expected. The oxidation potential during the following sweep became lower because dimer and oligomer can be oxidized at a lower potential, as suggested in the literature [22].

RESULTS AND DISCUSSIONS

In order to understand the copolymerization mechanism, different mole ratios of N-MPy and ECz were used for copolymerization and the resulting copolymers were characterized by various methods. Ceric ammonium nitrate was used in the chemical polymerization, frequently in pyrrole polymerization, because of its clean stoichiometry and oxidizing power.

The Effects of the Amounts of CAN and ECz on Chemical Polymerization

Figure 1 indicates that when CAN concentration increases, polymerization yield decreases. Moreover, new products of soluble oligomers ratio increase in solution. It is assumed that unlike the oxidizing power increase, the quantity of oligomer does not increase because the higher oxidizing power of CAN terminates the polymerization reaction. The maximum yield was found to be 63% for chemical polymerization. However, Figure 1 shows that as ECz concentration increases 4 times, it results in a decrease in yield from 41.55 to 29.15. Experiments were carried out with different initial mole ratios of $[\text{N-MPy}]_0/[\text{ECz}]_0$ at constant $[\text{ECz}]_0 = 0.02\,\text{M}$. Above a ratio of $n_{\text{N-MPy}}/n_{\text{ECz}} = 2$, the yield sharply decreases from 47.0 to 25.6%.

FT-IR Results

FT-IR reflectance spectra of products obtained by chemical polymerization are depicted in Figure 2. There are some differences between
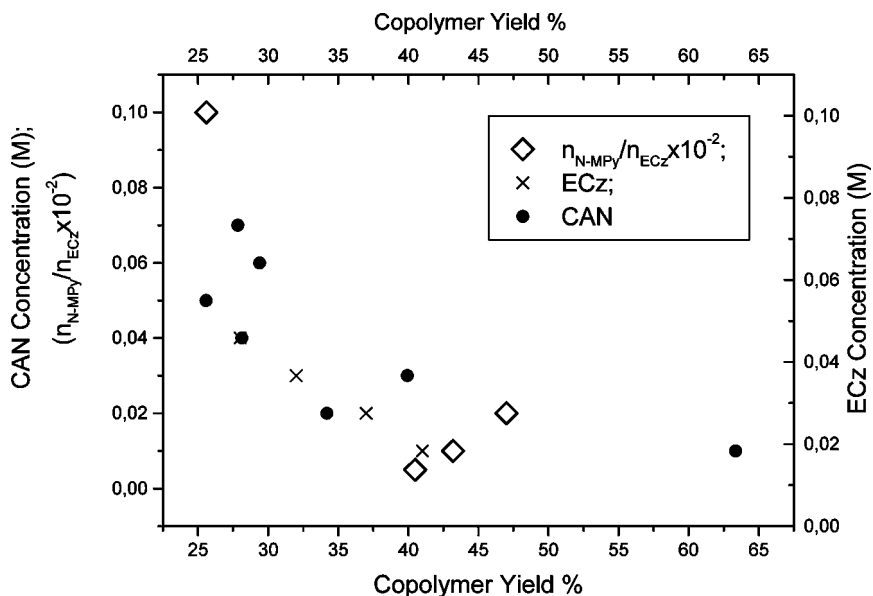

FIGURE 1 The effects of the amount of CAN[a], ECz[b] and copolymer mole ratio $(n_{\text{N-MPy}}/n_{\text{ECz}} \times 10^{-2})$[c] on the percent yield of chemical polymerization. (a: At constant concentrations of $[\text{ECz}]_0 = 0.03$; $[\text{N-MPy}]_0 = 0.06\,\text{M}$, b: $[\text{N-MPy}]_0 = 0.06$; $[\text{CAN}]_0 = 0.05\,\text{M}$, c: $[\text{ECz}]_0 = 0.02\,\text{M}$).
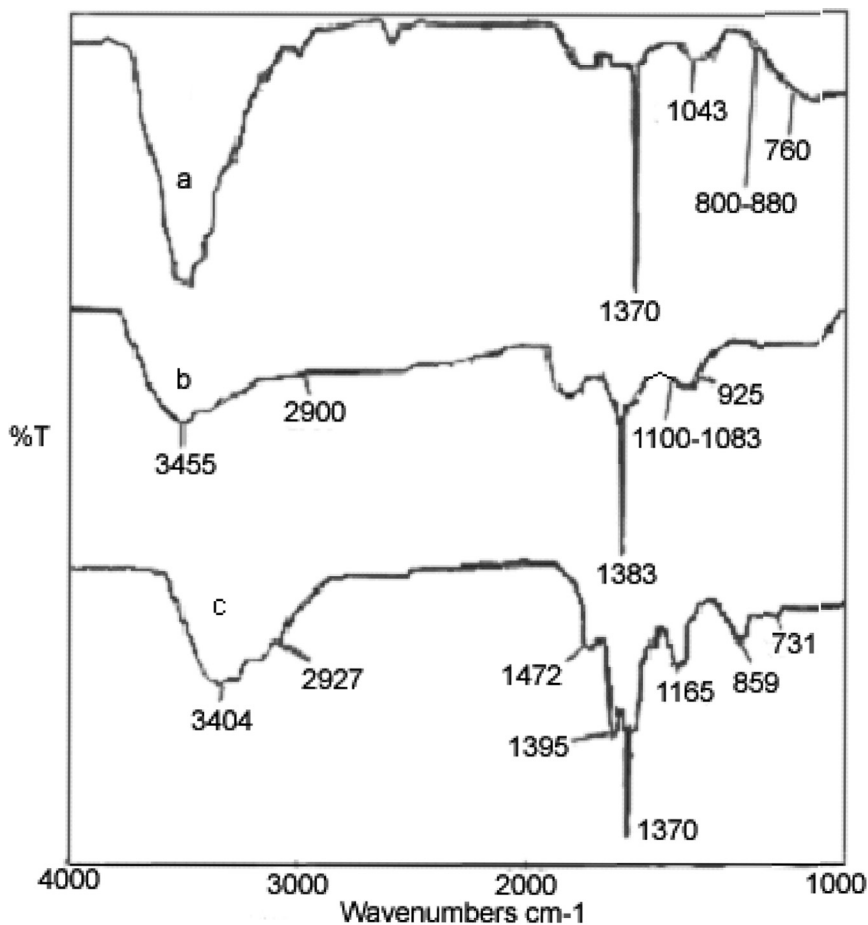
FIGURE 2 FT-IR spectra of (a) PECz; $[ECz]_0 = 0.03\,M$, $[CAN]_0 = 0.03\,M$, (b) PN-MPy; $[N\text{-}MPy]_0 = 0.06\,M$, $[CAN]_0 = 0.03\,M$,   (c) P[N-MPy-co-ECz], $[N\text{-}MPy]_0 = 0.06\,M$, $[ECz]_0 = 0.03\,M$, $[CAN]_0 = 0.03\,M$.

PECz, PN-MPy, and the copolymer spectra. The peak at $760\,cm^{-1}$ of FT-IR spectrum of PECzs shifted by $29\,cm^{-1}$ in FT-IR spectra of P[N-MPy-co-ECz]. The characteristic peak at $731\,cm^{-1}$ is caused by out of plane bending of C—H bond in benzene ring [29]. A significant band attributed to 1, 2, 4-trisubstituted benzene [37] appears, in the range 800–$859\,cm^{-1}$. The band around $2927\,cm^{-1}$ belongs to C—H bond of aliphatic groups. N—O band at $1370\,cm^{-1}$ proves CAN inclusion into the structure. A new peak appearing at $1395\,cm^{-1}$ is due to the bending of C—H bond. The presence of $1395\,cm^{-1}$ band due to C—CH$_3$

TABLE 1 Ratio of CAN Amount to C=C Peak Height in the FT-IR Spectrum of P[N-MPy-co-ECz] at Constant $[N-MPy]_0 = 0.06 \, M$, $[ECz]_0 = 0,03 \, M$

CAN. 10^2 mol. L^{-1}	CAN peak height to C=C peak height
3	4.55
5	10.88
7	11.75

bending of ECz testifies to the inclusion of ECz in the PN-MPy chain and that the pendant ethyl groups remained unaltered. The peaks at 1478, 1480, 1472 cm^{-1} are due to $-C=C$ stretching of benzene ring. The peak at 1348 cm^{-1} is because of the $C-N$ bond in benzene rings (due to ECz inclusion).

In the FT-IR spectrum of the obtained copolymers, the ratio of CAN peak height to C=C peak height showed that increase of CAN concentration resulted in an increase in that ratio (Table 1) and more oligomers formation. UV-Vis spectrum of P[N-MPy-co-ECz] indicated that there are some shifts in the peak potentials compared to homopolymers, which supports copolymer formation. If the amount of CAN raised up, the percentage of CAN incorporated in the copolymer structure increased. The intensity of the band (at 760 cm^{-1}) in comparison to monomer spectra, which is due to $-C-H$ out of plane deformation, in dark green colored polymer spectrum, confirms the incorporation of ECz in the copolymer structure [31]. Decreasing intensity of this peak showed that the polymerization occurs through the ring.

UV-Vis Spectrophotometric Results

Ex-situ spectrophotometric measurement was carried out to characterize P[N-MPy-co-ECz] obtained by chemical polymerization. In the case of PN-MPy, these maximum absorption peaks are 821, 438, and 365 nm. The maximum absorption peaks of PECz at 811 nm can be assigned from the bonding level to anti-bonding state of polaron, a polaron bonding level to the Π^* conduction band and a valence band to conduction band, respectively [35–36]. Furthermore, soluble portions of the oligomers are observed in solution after obtaining the products. As a solution, P [N-MPy-co-ECz] characteristic peaks are observed at 853, 660, and 484 nm. In case of copolymer, the characteristic peaks of P[N-MPy-co-ECz] shifted with comparison to homopolymers.
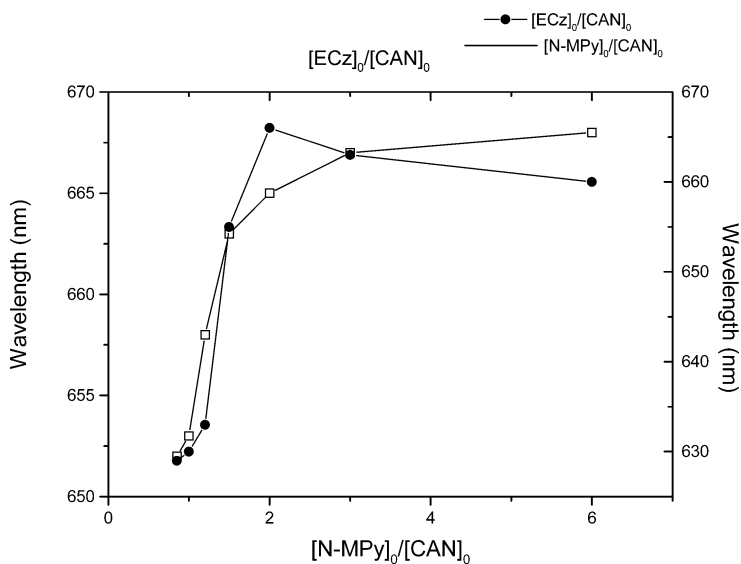
FIGURE 3 In chemical [N-MPy] and ECz copolymerization, $[N-MPy]_0/[CAN]_0$ and $[ECz]_0/[CAN]_0$ vs. wavelength, processed at constant $[ECz]_0 = 0.03 \, M$ and $[N-Mpy]_0 = 0.06 \, M$.

Moreover, UV-visible absorption spectra results (Figure 3) indicate that with an increase in the ratio of $[N-MPy]_0/[CAN]_0$, the wavelength shifts to higher values from 652 to 668 nm whereas when the ratio of $[ECz]_0/[CAN]_0$ increases, the wavelength shifts from 652 to 665 nm. This is due to the increase in conjugation of copolymer so that the wavelength shifts to higher values.

Electrochemical Polymerization

For electrochemical polymerization an alkyl-substituted monomer of Py and Cz, namely N-MPy and ECz, were used. In order to understand the reaction of polymer and copolymer film formation, cyclic voltammograms were carried out and current versus potential curves were plotted. In the first cycle, N-MPy was oxidized to the radical cation form, and N-MPy/ECz was copolymerized (in different mole ratios) by electrochemical process (Figure 4). Peak currents (which are related to charge) increase linearly with scan number, therefore increase in charge (Q) results in the formation of more radical ions (R^+), and more copolymer formation. Slope of lines of current versus scan rate (or charge) of copolymer seems to be additive.
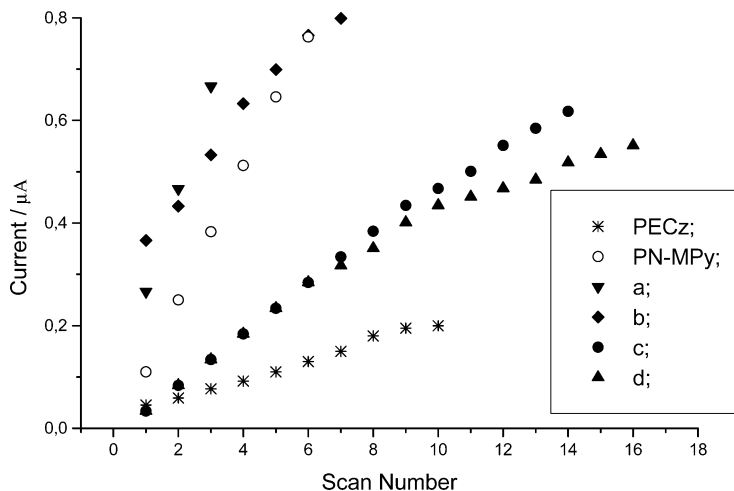
FIGURE 4 Current vs. scan number graph obtained during polymer growth for PN-MPy, PECz, and P[N-MPy-co-ECz] (scan rate $100 \, mVs^{-1}$, 0–1.2 V vs. Ag). Cyclic voltammogram of P[N-MPy-co-ECz] electrochemically polymerized from mixture of N-MPy-ECz at a mol ratio of (a: $n_{N\text{-}MPy}/n_{ECz} = 5$; b: $n_{N\text{-}MPy}/n_{ECz} = 10$; c: $n_{N\text{-}MPy}/n_{ECz} = 1$; d: $n_{N\text{-}MPy}/n_{ECz} = 2$) in 0.1 M NaClO$_4$/ACN solution using multiple (eight cycles).

P[N-MPy-co-ECz] was obtained electrochemically in 0.1 M NaClO$_4$ electrolyte on Pt. Cyclic voltammograms of copolymers and homo-polymers were obtained at different mol ratios that in the mol ratio of ($n_{N\text{-}MPy}/n_{ECz} = 5$) has higher current value than that of ($n_{N\text{-}MPy}/n_{ECz} = 10$). In addition, the mol ratio of ($n_{N\text{-}MPy}/n_{ECz} = 1$) has higher current value than that of ($n_{N\text{-}MPy}/n_{ECz} = 2$) (Figure 4).

Scan rate dependence of homopolymer and copolymer films in monomer-free electrolyte were obtained (Table 2) and a direct propor-tionality of peak anodic and peak cathodic currents to the square root of the scan rate was found which suggests a diffusion-controlled electrochemical redox process. Oxidation potential corresponding to N-MPy/ECz mixture increased to 1100 mV with respect to monomers. Also, a copolymer peak potential at 550 mV was found in-between the PN-MPy and PECz peak potentials.

A tentative mechanism for chemical and electrochemical polymeri-zation of methylpyrrole and ethylcarbazole is suggested (Scheme 1). The electron transfer from monomer to electrode results in a radical cationic species of methylpyrrole during the electrogrowth process, where coupling and dehydrogenation of two radical cationic species

TABLE 2 Half Wave Potentials, Anodic and Cathodic Peak Potentials in Monomer Free Electrolyte Obtained from CV

Polymer (25°C)	E_a^2, V	$E_{1/2}$, V	ΔE, V	E_a^1, V	E_c, V
PECz	0.99	0.51	0.38	0.70	0.32
PN-MPy	0.87	0.26	0.13	0.32	0.19
P[N-MPy-co-ECz][a]	1.10	0.39	0.32	0.55	0.23
Copolymer at different Temp. (°C)	E_{onset},V	$E_{1/2}$, V	ΔE, V	E_a, V	E_c, V
−7	0.46	0.39	0.33	0.56	0.23
−5	0.52	0.43	0.17	0.52	0.35
0	0.53	0.43	0.22	0.54	0.32
10	0.55	0.37	0.37	0.55	0.18
20	0.51	0.36	0.32	0.52	0.20
30	0.50	0.41	0.18	0.50	0.32

*Given potentials have deviation $= \pm 0.003$ V.

[1]Polymer oxidation potential, V.

[2]Monomer oxidation potential, V.

[a]Initial feed ratio of monomers, $n_{N\text{-}MPy}/n_{ECz} = 2$.

bring about chain growth. Becasuse the rate of polymerization of ECz seems to be higher than N-MPy (according to current values obtained for homopolymers at the same conditions), to balance the rate of polymerization of N-MPy and ECz, the initial amount of N-MPy in the feed was greater than ECz.

P[N-MPy-co-ECz] and homopolymers were obtained electrochemically in 0.1 M TBAP/ACN solution using a multiple of eight cycles. Only the fourth cycle on Pt electrode is illustrated in Figure 5. Oxidation potential of the copolymer decreased to 0.55 V (smaller than PECz = 0.70 V). CV of copolymer growth indicated that the copolymer shows different redox behavior than the homopolymers. At 30°C and −5°C the polymer showed more reversible behavior ($\Delta E = 0.18$ V) than the others (Table 2). The copolymer was studied potentiodynamically at different temperatures and the maximum current was obtained at 30°C. Thus, the optimal temperature can be taken as 30°C (Figure 6).

Changing the sweep rate at which the polymers were grown appears to have an effect on the growth mechanism, as shown in Scheme 1. The polymers were formed at different sweep rates 300, 200, 100, 50 mVs^{-1} and then cycled in a monomer free solution at 100 mVs^{-1} for 8 cycles. In monomer free solution, the CV of P[N-MPy-co-ECz] formed at 100 mVs^{-1} indicates that during the first few cycles, oligomeric species or small polymer chains dissolve during the oxidation and reduction cycle, leaving behind longer polymer chains that remain adhered. Therefore, the charge stabilizes after a
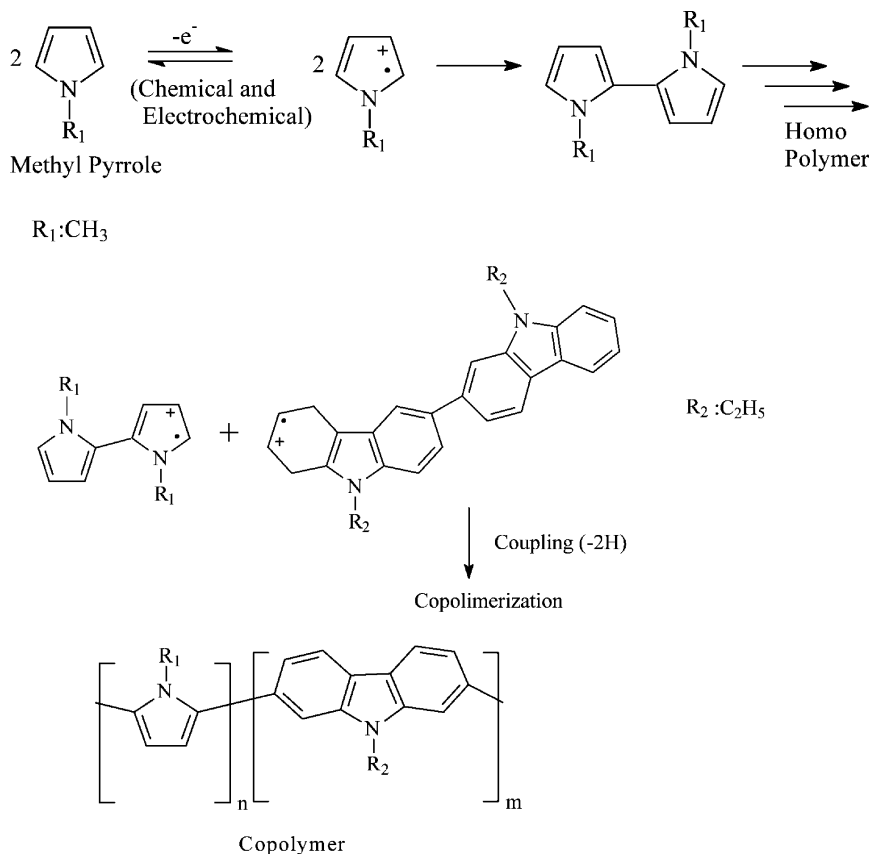
SCHEME 1 A tentative mechanism for chemical and electrochemical polymerization.

few cycles. This dissolution of smaller species was not observed for the polymers formed at slower rates, indicating that longer chains were obtained at slow rates, allowing a more stable structure of the polymer.

The maximum charges were obtained in anodic peak currents of P[N-MPy-co-ECz] during the polymer growth in various electrolytes $0.1 M$ LiClO$_4$ in PC at $100 mVs^{-1}$ (Figure 7). In parallel to these data, PC exhibits the highest dielectric constant (ϵ of PC = 66.14; DMF = 38.25; ACN = 36.64). Although LiClO$_4$ in PC has highest currents, NaClO$_4$ in DMF solution has low currents probably due to solubility of the polymer in DMF (Figure 7).
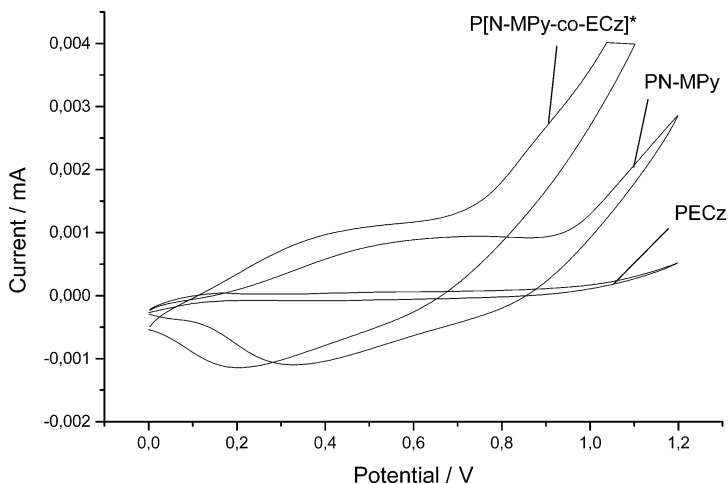
FIGURE 5 Electrochemical coating of PN-MPy, PECz, P[N-MPy-co-ECz] by CV in 0.1 M TBAP/ACN solution using multiple (eight cycles) and taken fourth cycle. (Scan rate: $100\,mVs^{-1}$, 0–1.2 V vs. Ag) $[\star] = (n_{N\text{-}Mpy}/n_{ECz} = 1)$; $[N\text{-}Mpy]_0 = 0.01\,M$, $[ECz]_0 = 0.01\,M$.
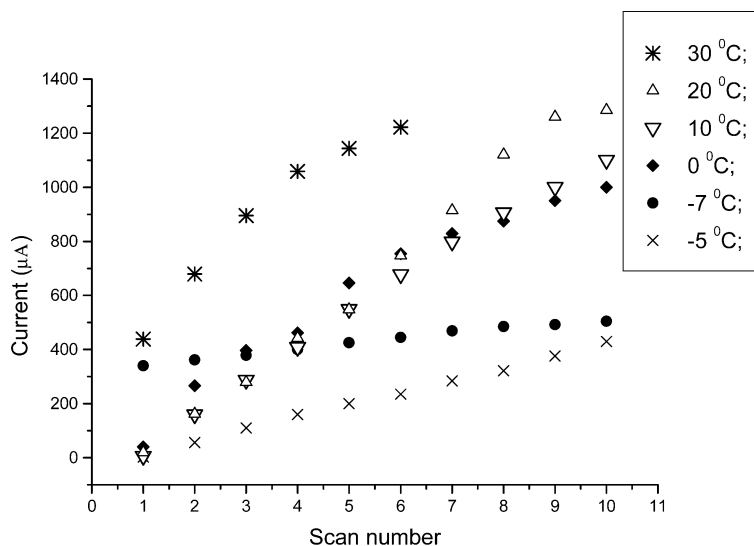

FIGURE 6 Anodic peak currents of P[N-MPy-co-ECz] during polymer growth in different temperatures ($-7°C$; $-5°C$; $0°C$; $10°C$; $20°C$; $30°C$), at concentrations $[EC_Z]_0 = 0.01\,M$ $[N\text{-}MPy]_0 = 0.01\,M$, in 0.1 M NaClO$_4$/ACN solution using multiple (ten) cycles at $100\,mVs^{-1}$.
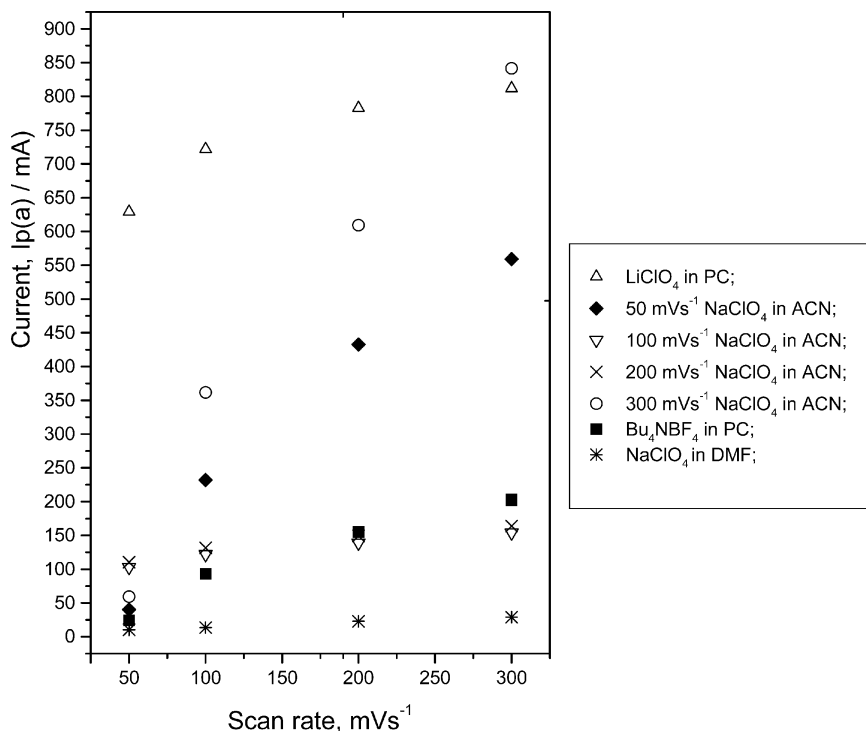
FIGURE 7 Anodic peak currents of P[N-MPy-co-ECz] during polymer growth in different electrolytes, $LiClO_4$ and Bu_4NBF_4 in PC, $NaClO_4$ in ACN and DMF and scan rates 50, 100, 200, 300 mVs^{-1} vs. dielectric constants (ϵ).

CONCLUSIONS

The chemical and electrochemical polymerization of N-MPy and ECz has been investigated in this study. In chemical polymerization, as the CAN and ECz concentrations increase, the copolymerization yield decreases (Figure 1). Different mol ratios of N-MPy and ECz were used at constant ECz and it was found that above at a mol ratio of $(n_{N\text{-}MPy}/n_{ECz} = 2)$ the yield decreases sharply. Although an increase of CAN increases the oxidizing power, the amount of copolymer does not rise and remains in soluble level by termination process in solution. FT-IR results of copolymers have shown new bands and some peak shifts compared to homopolymers.

Cyclic voltammograms of copolymers and homopolymers were obtained at different mol ratios and the highest current value was obtained for $n_{N\text{-}MPy}/n_{ECz} = 5$ monomer feed ratio. It has been observed

that when ECz is copolymerized with N-MPy, the electrochemical properties of PECz are improved. A tentative mechanism was proposed for chemical and electrochemical polymerization of methyl pyrrole with ethyl carbazole.

The choice of solvent, temperature, and supporting electrolyte has a large influence on the electropolymerization behavior, with propylene carbonate being the best solvent of those tested having a high dielectric constant, and resulting in a high current value. The polymerization rate was found to be faster in $LiClO_4$ than $NaClO_4$ and Bu_4NBF_4 (Figure 7). In this article, it was demonstrated that the copolymer coating of platinum could be modified by electrochemical polymerization, under different mole ratio, sweep rate, supporting electrolyte type, and temperature conditions.

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