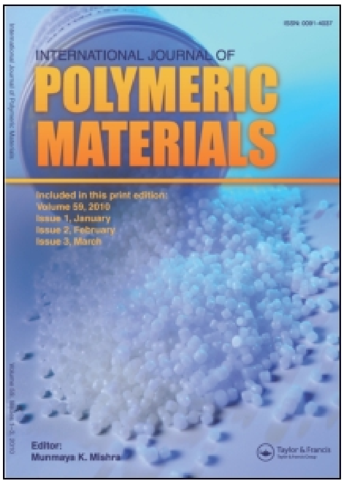

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Electrochemical copolymerization of Carbazole, Ethylcarbazole and N-Vinylcarbazole with methyl ethyl ketone-formaldehyde resin

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To cite this Article Ustamehmetoğlu, Belkis , Kizilcan, Nilgün , Saraç, A. Sezai and Akar, Ahmet(2005) 'Electrochemical copolymerization of Carbazole, Ethylcarbazole and N-Vinylcarbazole with methyl ethyl ketone-formaldehyde resin', International Journal of Polymeric Materials, 54: 3, 161 — 172

To link to this Article: DOI: 10.1080/00914030390207246

URL: http://dx.doi.org/10.1080/00914030390207246

International Journal of Polymeric Materials, 54:161–172, 2005
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390207246

ELECTROCHEMICAL COPOLYMERIZATION OF CARBAZOLE, ETHYLCARBAZOLE AND N-VINYLCARBAZOLE WITH METHYL ETHYL KETONE-FORMALDEHYDE RESIN

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Electrochemical polymerization of carbazole (Cz), N-Vinylcarbazole (NVCz), and Ethylcarbazole (ECz) in the presence of methyl ethyl ketone formaldehyde resin (MEKF-R) was accomplished by using acetonitrile-NaClO$_4$ solution. The effects of monomer and resin concentration were investigated on the conductivity of the resulting products. Characterization of insoluble free standing films was carried out via FTIR spectrum, cyclic voltammogram, UV visible spectrum, four point probe conductivity measurements, and elemental analyses. The conductivities of the copolymers were in the range of $10^{-6}-10^{-4}$ S/cm. All copolymers obtained electrochemically were insoluble in solvents.

Keywords: electrochemical polymerization, carbazole, N-Vinylcarbazole, ethylcarbazole, methyl ethyl ketone formaldehyde resine, conductive polymers

INTRODUCTION

Recently carbazole−based polymer systems have received considerable attention, which is amply justified in view of the unusual electrical, photoelectric, thermal, and other relevant properties of these materials [1]. But far fewer articles have described the electrodeposition of films from carbazole and their properties [2−5] than polyaniline [6] polythiophene [7] and polypyrrole [8]. On the other hand anodic

Received 14 January 2003; in final form 5 March 2003.

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oxidation of N-ethylcarbazole in acetonitrile does not produce films [2] except on Au and glassy carbon electrodes in aqueous $HClO_4$ with conductivities of between 10^{-8} and 10^{-4} S/cm [9].

The electrical conductivity of polycarbazoles has been found to be quite smaller than that obtained with the more classical conductive polymer [10]. Beside this, polcarbazoles have limited solubility in most solvents and cannot be characterized by conventional methods [11]. Attempts have been made at composite formation with different polymer matrices [9] and at the copolymerization with heterocyclic monomers [12] with the aim of improving the conductivity of the resulting product. To overcome the solubility problem, oxidative polymerization of N-Vinylcarbazole in polymer matrix has been carried out [13]. Unfortunately, the polymer stays in colloidal form or is obtained as ternary complexes. Recently, an electrochemical study of soluble copolymer of ethylcarbazole with N-methyl pyrrole and 3-Methyl thiophene has been reported [14].

The addition of ketonic resin to the polymerization media resulted in soluble and conductive copolymers of polypyrrole and polycarbazoles in the chemical polymerization [15, 16]. However, electropolymerization of pyrroles and ketonic resin resulted in insoluble copolymers [17] and has optical and conductive properties similar to PPy. In order to extend this work, Cz, ECz, and NVCz are electrochemically copolymerized with MEKF-R and compared with their chemically copolymerized counterparts.

EXPERIMENTAL

Materials

Methl ethyl ketone formaldehyde resin (MEKF-R) was prepared according to Reference [15]. Carbazole (Cz), N-vinylcarbazole (NVCz), ethylcarbazole (ECz), acetonitrile, dimethyl-formamide (DMF), acetone, and ceric ammonium nitrate (CAN) were all Merck reagent grade chemicals of the highest purity and used without further purification. All solutions were prepared fresh before each run.

Analyses

Infrared (IR) spectra were recorded on a JASCO FTIR 5300 Fourier transform infrared spectrometer.

Electrical conductivities of the solid products and solutions were measured by using four point probe technique and WTW Microprocessor type conductometer respectively.

Potentiodynamic electrodeposition was performed with a potentiostat Wenking POS 73 model in conjugation with X-Y recorder (Kipp and Zonen).

Elemental analyses were done with Carlo Erba 1106 Elemental Analyzer.

Chemical Polymerization of MEKF-R/Carbazole Copolymers

First MEKF-R, CAN, and Cz or ECz were dissolved in acetonitrile seperately. Then, CAN solution was added dropwise to the mixture of MEKF-R and Cz solution while stirring. A green powder formed almost instantaneously. After one hour at 25°C, the precipitated powder was filtered, washed with acetonitrile, and dried at room temperature.

Electrochemical Preperation of MEKF-R/Carbazoles Copolymers

The electrochemical synthesis of the polymers was performed at a constant voltage of 1.2 V. Pt electrodes were used as a counter and a working electrode and Ag wire as a reference. The polymerization solution consisted of acetonitrile solution containing 0.1 M of $NaClO_4$ as electrolyte and both monomer and resin. The monomers were Cz ECz, and NVCz. Stainless steel plates were used as electrodes (10 cm^2); 3 V was applied for one hour. The polymers were recovered as green films on electrodes and washed with acetone and dried at room temperature.

Two Step Copolymerization of N-Vinyl Carbazole (NVCz)

Vinyl Copolymerization

First, the colorless and insulator from of NVCz/MEKF-R compolymer obtained from the chemical polymerization of NVCz through only the vinyl group was polymerized using molar ratio of n_{CAN}/n_{mon} lower than 0.2. The total volume was 60 ml in all experiments. After filtration, the copolymer was washed with acetonitrile, and the white powder was dried, dissolved in dichloromethane and oxidized further via the carbazole rings either with Ce(IV) or electrochemically.

Further Oxidation Via the Carbazol Rings

Oxidation with Ce(IV)

The colorless, insulator copolymer was converted into green, conductive copolymer by further addition of CAN solution to the colorless copolymer dissolved in dichloromethane. The polymer mixture obtained by this method (colorless copolymer and green, further oxidized product) was separated by dissolving the colorless vinyl copolymer in toluene. The green copolymer, however, was insoluble in toluene and was thus filtered off and the mother liquor was reprecipitated in an excess of methanol.

Electrochemical Oxidation

The conventional three electrode system was used for further oxidation of the colorless copolymer electrochemically. The anode was a Pt disk (area: 0.2 cm^2), the cathode was a saturated calomel electrode (SCE) connected to the measuring solution by a Luggin capillary via a salt bridge. A Wenking POS 73 Model Scanning potentiostat was employed for the electrolysis. The conducting PolyNVCz/MEKF-R was formed as a dark green film on the Pt electrode surface in an acetonitrile solution containing 0.1 M $NaClO_4$. 1.6 Volt was applied in this system to the colorless copolymer dissolved in dichloromethane and a green conductive form of the copolymer was obtained on the electrode surface. It was washed with acetone and dried in room temperature.

Conductivity Measurements

In order to measure the electrical conductivity, the polymers were compacted under 10 tons pressure to obtain thin pellets. Typical sample dimensions were 13 mm diameter and 0.8 mm thickness. Conductivity measurements were performed by the use of Four-Probe Technique and calculated from the following equation:

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

where V is the potential in volts, I is current in amper, and dn is the thickness in cm.

Elemental Analyses

Although the MEKF-R content was changed from 0.001 to 0.001 M, the C, H, and N content of all of electrochemically produced Cz/MEKF-R copolymers were about 60%, 4%, and 4%, respectively. This might be due to a low amount of resin inclusion in the PCz chain.

RESULT AND DISCUSSION

Electrochemical Characterization

In order to investigate the Cz-Resin interaction and resulting product on the electrode surface, current-potential curves of Cz and mixture of Cz/MEKF-Resin in acetonitrile were taken separetely at a potential sweep rate of 20 mV/s. They are given in Figures 1 and 2, respectively. The measurements were carried out with ascending anodic potentials. The anodic current increased with the cycle number for Cz, and Cz/MEKF-R mixture. The CV of the PCz/MEKF-R and PNVCz/MEKF-R

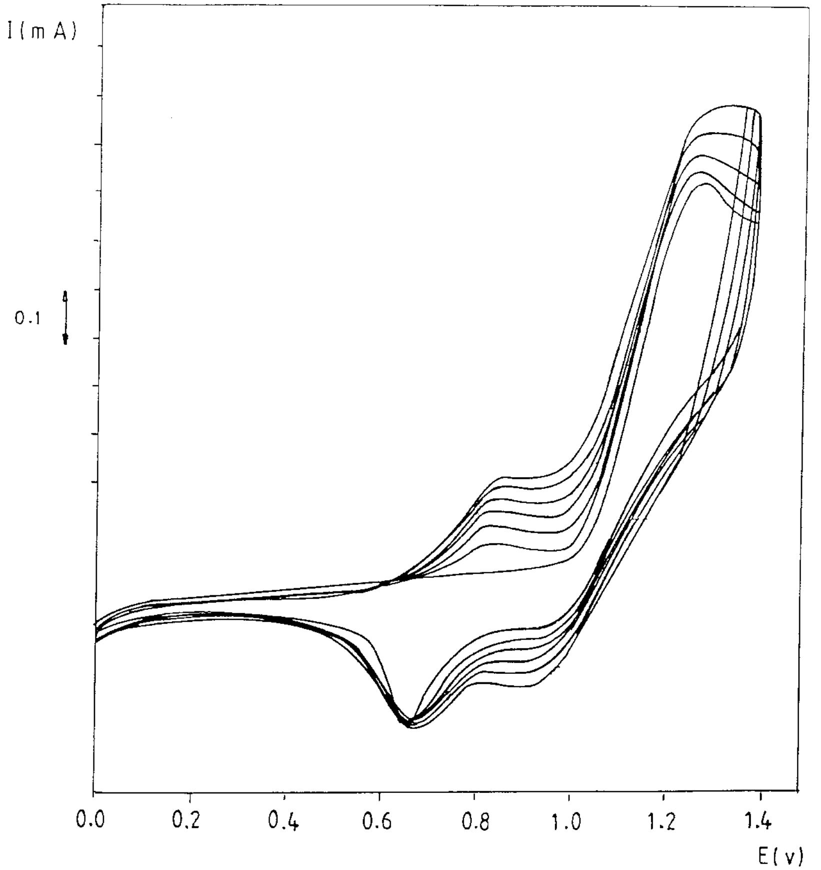

FIGURE 1 I-E curves of Pt electrodes in the presence of 0.01 M Cz in acetonitrile containing 0.1 M Sodium percholorate during the anodic oxidation (potential sweep rate of 20 mV/s).

coated electrodes were taken between 0.0 and 1.2 V in fresh electrolyte at a scan rate of 20 mV/s (Figures 3 and 4, respectively). The curve 2 concern current-potential curves (I-E curve) for electropolymerization of the mixture of monomer and resin. Decreasing current value in the presence of resin (curve 2) comparing PCz or PNVCz homopolymers

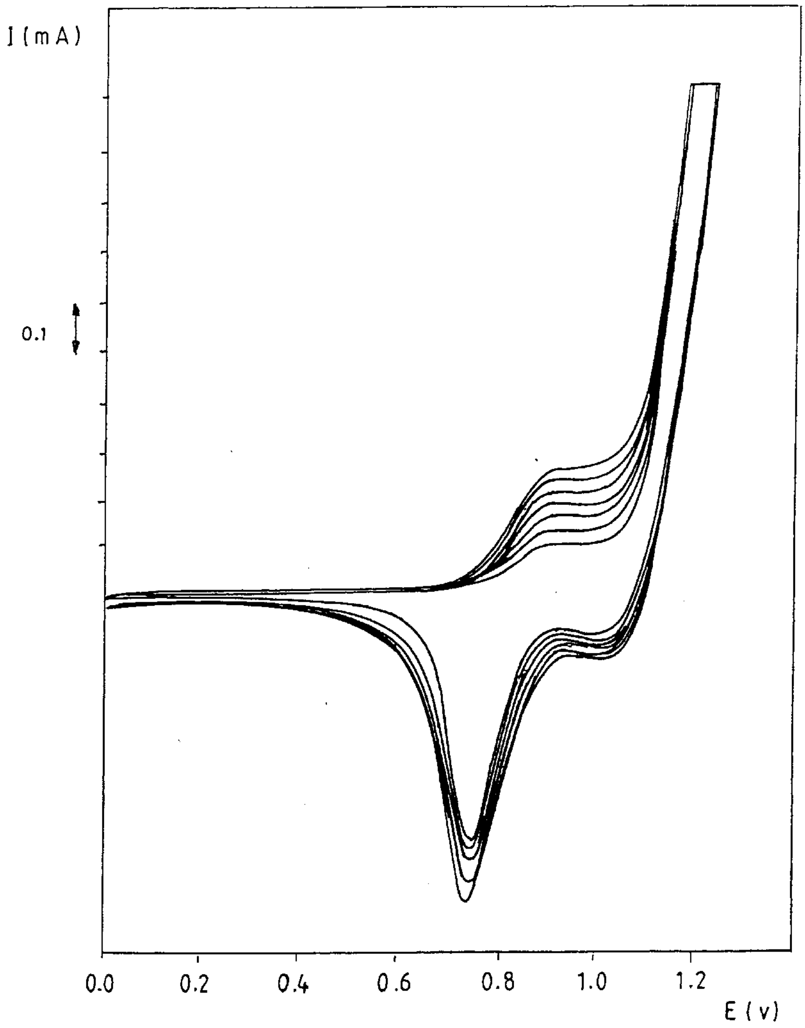

FIGURE 2 I-E curves of Pt electrodes in the presence of 0.01 M Cz and 0.01 M MEKF-R in acetonitrile containing 0.1 M Sodium percholorate during the anodic oxidation (potential sweep rate of 20 mV/s).

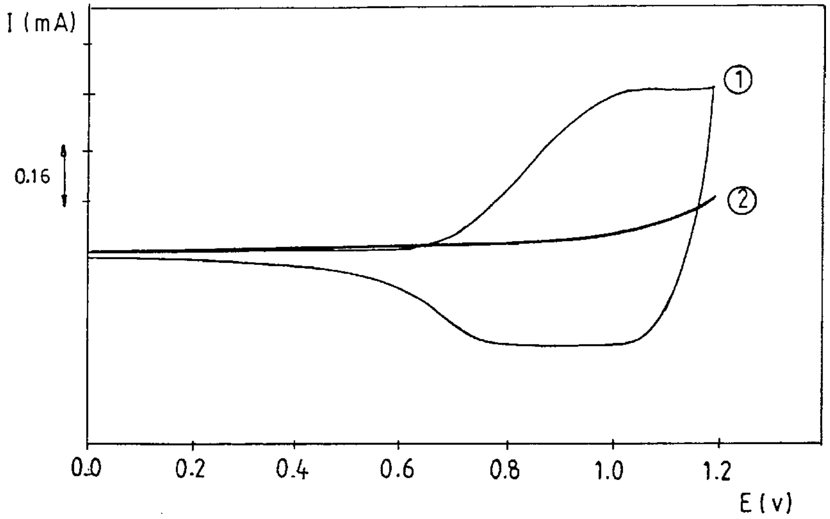

FIGURE 3 CV of coated electrodes in an acetonitrile soultion containing 0.1 M Sodium percholorate at a potential sweep rate of 20 mV/s. 1-PCz electrode, 2-PCz/MEKF-R Copolymer electrode.

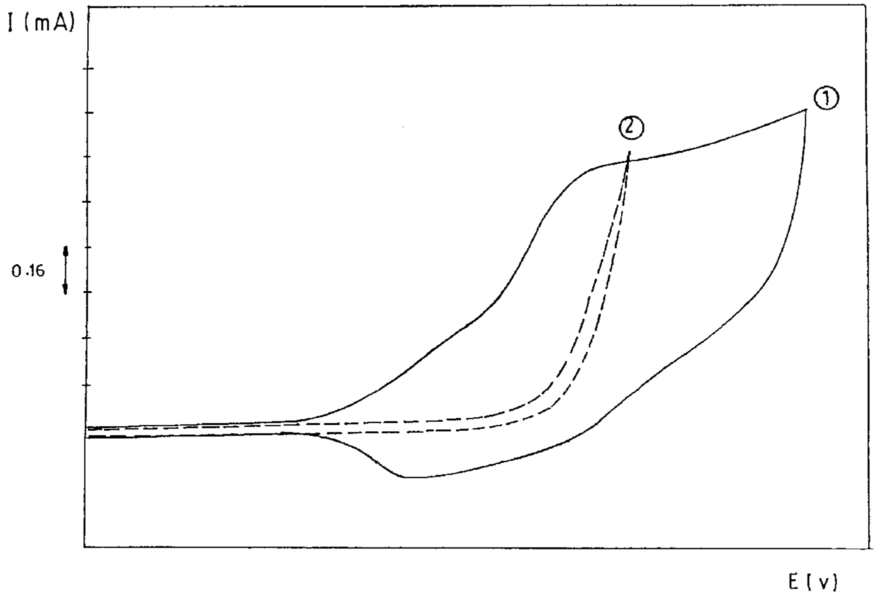

FIGURE 4 CV of Coated electrodes in an acetonitrile solution containing 0.1 M Sodium percholorate at a potential sweep rate of 20 mV/s. 1-PNVCz electrode, 2-PNVCz/MEKF-R Copolymer electrode.

electrodes (curve 1) supports the notion that the resin was incorporated in the resulting polymer coatings.

The Effect of Monomer on the PCz/MEFK-R, PECz/MEKF-R, and PNVCz/MEKF-R Copolymers

The electrical conductivity of homopolymers depends on the type of carbazole monomer (Table 1).

The Conductivity of the copolymers changes with monomer type used, both in chemical and electrochemical polymerization. The higher conductivity of the copolymer in electrochemical synthesis was obtained by using Cz in the presence of MEKF-R. Chemical polymerization of ECz by CAN gives the advantages of obtaining PECz with high conductivities although the anodic oxidation of Ecz does not produce films on the electrode surface in acetonitrile [5]. Obtaining polymer film in the presence of MEKF-R indicates the MEKF-R inclusion to the Polyethylcarbazole chain. The conductivity of the resulting copolymer was 2.6×10^{-6} S/cm. The copolymer is obtained only if MEKF-R/Ecz ratio is higher than 1.

The Effect of MEKF-R on the Conductivity of PCz/MEKF-R Copolymers

The Conductivity of the copolymers changes with mole ratio of MEKF-R/Cz as seen in Table 2. Because the conductivity of the resin is very low, the decreased conductivity is due to MEKF-R segments in the copolymer chains.

The Effect of Polymerization Type on the Conductivity of PNVCz/MEKF-R Copolymers

As seen in the Table 3, the conductivity of electrochemically produced PNVCz/MEKF-R copolymers was similar to the homopolmer if the first step is chemical copolymerization (Table 3, Nos. 2 and 5).

FT-IR Results

The FT-IR Spectrum in of PCz electrochemically prepared in the presence of MEKF-R is shown in Figure 5a. The spectrum of PCz/MEKF-R copolymer has different characteristics than PCz and MEKF-R (Figure 5b) seperately. As a blank experiment, MEKF-R was electrolyzed at the same conditions as electrochemically synthesized copolymer for 15 min (Figure 5c). The absence of carbonyl peak at

TABLE 1 The Effect of Monomer on the Chemically and Electrochemically Synthesized Products

				Conductivity (S/cm)	
Cz Mol/l	ECz Mol/l	NVCz Mol/l	MEKF-R Mol/l	Electrochemical	Chemically
0.12	—	—	8.6×10^{-3}	8.5×10^{-4}	8.8×10^{-4}
—	0.12	—	8.6×10^{-3}	—*	2.0×10^{-5}
—	—	0.12	8.6×10^{-3}	5×10^{-5}	1.9×10^{-3}
0.12	—	—	—	6.2×10^{-2}	4.4×10^{-3}
—	0.12	—	—	—*	1.8×10^{-4}
—	—	0.12	—	4.2×10^{-4}	2.2×10^{-3}
1.55×10^{-2}	—	—	3.1×10^{-3}	2.18×10^{-4}	—**
—	1.55×10^{-2}	—	3.1×10^{-3}	—*	—**
—	—	1.55×10^{-2}	3.1×10^{-3}	1.2×10^{-4}	—**
—	1.55×10^{-2}	—	1.63×10^{-2}	2.6×10^{-6}	—**
—	—	—	1.63×10^{-2}	—*	1×10^{-7}

[CAN] = 0.06 M; *No polymer was formed; **Pellets could not be prepared from sticky products.

TABLE 2 The Effect of MEKF-R Content on the Conductivity of Copolymers of Carbazole Produced Electrochemically

Cz Mol/l	MEKF-R Mol/l	$N_{MEKF\text{-}R}/n_{Cz}$	Conductivity (S/cm)
1.55×10^{-2}	0	—	2.21×10^{-3}
1.55×10^{-2}	1.55×10^{-3}	0.1	5.04×10^{-4}
1.55×10^{-2}	3.1×10^{-3}	0.2	2.18×10^{-4}
1.55×10^{-2}	6.2×10^{-3}	0.4	4.08×10^{-5}
1.55×10^{-2}	1.55×10^{-2}	1.0	8.80×10^{-6}
0	1.55×10^{-2}	—	1.00×10^{-7}

about 1700 cm^{-1} in the spectrum of the copolymer and the product obtained in blank experiment suggests that MEKF-R has a different structure than its original structure in the copolymers.

Thermal Analyses

MEKF-R and PCz/MEKF-R have Tm value of 90°C and 77°C, respectively. Because it is known that conductive polymers have no Tm and Tg values, Tm values of electrochemically produced PCz/MEKF-R copolymers is due to segments introduced by ketonic resin.

CONCLUSION

Copolymers of carbazoles, such as carbazole, ethyl carbazole, and vinyl carbazole, with MEKF-R were synthesized for the time eletrochemically. Inclusion of the ketonic resin resulted in copolymers with lower conductivities. These polymers had crystalline region with a

TABLE 3 Conductivity Differences of PNVCz/MEKF-R Copolymers Due to the Polymerization Route

No.	Polymer	Chemical	Electrochemical	Color	Conductivity (S/cm)
1	PNVCz	+		white*	—
2	PNVCz		+	green	2.7×10^{-4}
3	PNVCz/MEKF-R	+		white*	—
4	PNVCz/MEKF-R	+		green**	1.91×10^{-3}
5	PNVCz/MEKF-R		+	green***	1.2×10^{-4}
6	PNVCz/MEKF-R		+	green	5.1×10^{-5}

*n_{CAN}/n_{mon} is lower than 0.2; **n_{CAN}/n_{mon} is higher than 0.2; ***Electrochemical oxidation product of polymer No: 3.

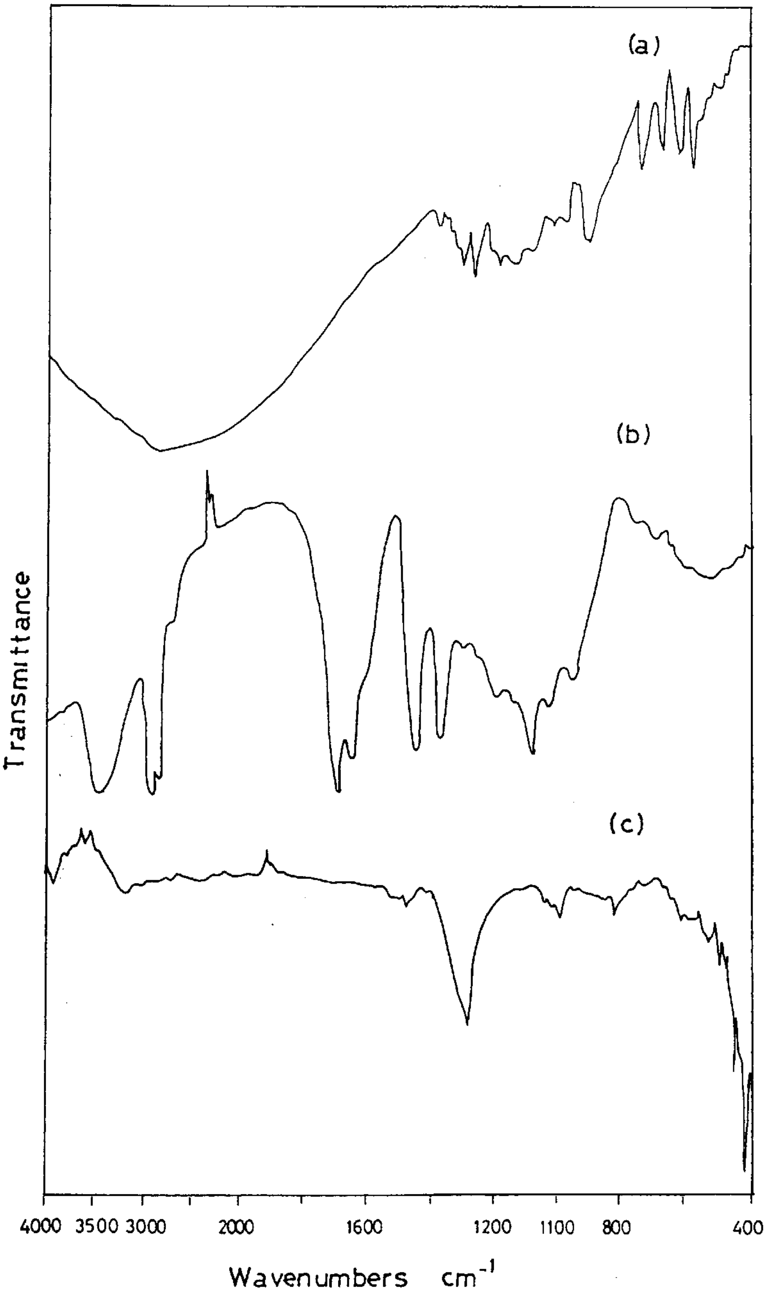

FIGURE 5 FT-IR spectra of PCz/MEKF-R copolymer (a), MEKF-R alone (b), and MEKF-R after electrolysis at 1.6 V for 15 min (c).

melting point of 77°C. Besides, electrochemical polymerization of ECz was achieved by this copolymerization method. Even though having lower conductivity of the copolymers than their homopolymers counterparts, the copolymers may find an increasing area of their applications due to the presence of crystalline region in their structure.

The difference of current values of homopolymers and copolymers coated electrodes in the I-E curves depended on the carbazole type used. Copolymer electrodes showed reversible electrochemical behavior.

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