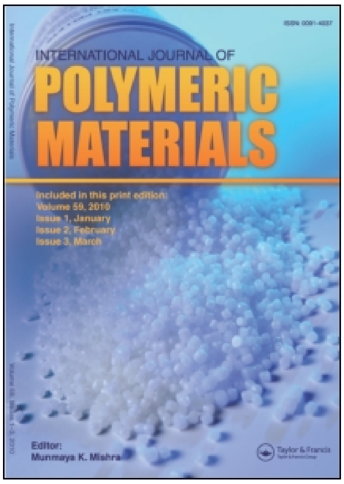

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Electrochemical Copolymerization of Pyrrole and Methyl Ethyl Ketone Formaldehyde Resin

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Electrochemical polymerization of pyrrole in the presence of methyl ethyl ketone formaldehyde resin (MEKF-R) was accomplished. Characterization of insoluble free-standing films was carried out via FTIR spectrum, cyclic voltammogram (CV), UV-visible spectrum, and four-point probe conductivity measurements. The effect of pyrrole and the resin concentrations on the conductivity of the resulting products was investigated. The copolymers obtained as free-standing films have conductivity value of 10^{-6}–10^{-2} *S/cm and they are insoluble in organic solvents.*

Keywords: electrochemical polymerization, pyrrole, methyl ethyl ketone formaldehyde resin, conductive polymers

INTRODUCTION

Electrically conducting polymers made from heterocyclic monomers have been the subject of many research areas such as photogalvanic cells [1], membrans [2], biosensors [3], binding and release of metallic cations [4], electrochromic devices [5], and gas sensors [6].

Polypyrrole (PPy) has been the focus of these studies partly because it can be prepared by both electrochemical [7] and chemical oxidation [8] and partly because of its relatively good stability. A polypyrrole free-standing film is hard and brittle, difficult to handle, and it is insoluble in common solvents. The poor mechanical properties of PPy greatly restrict its potential for applications.

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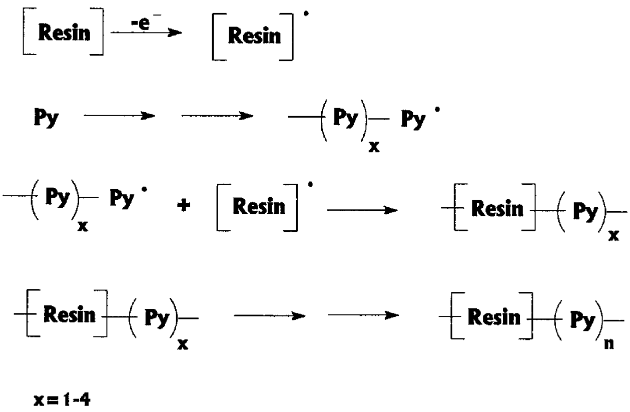

SCHEME 1 Proposed polymerization mechanism.

The structure of PPy and the polymerization mechanism have not been well defined. The initial step in the electropolymerization of pyrrole is thought to be formation of unstable pyrrole radical cations, which dimerize with the expulsion of $2H^+$ in the proposed mechanism [9]. The second mechanistic possibility in the initiation step is the proton loss of radical cation to form a radical that attacks a pyrrole molecule [10]. Redox reaction between MEKF-R and Ce(IV) was previously used for copolymer formation [11]. A similar method was used for copolymerization of pyrrole with silicon oligomers [12]. The present authors have recently reported that both soluble and conducting PPy could be produced by oxidation of pyrrole with Ce(IV) in the presence of methyl ethyl ketone formaldehyde resin (MEKF-R) [13]. A mechanism of polymerization was proposed as shown in Scheme 1. A resin molecule loses an electron to form a radical that combines with a growing PPy chain.

These studies have now been extended to include electrochemical production and spectroelectrochemical investigation of these copolymers, and to compare their physical properties such as solubility and conductivity.

EXPERIMENTAL

Materials

Methyl ethyl ketone formaldehyde resin (MEKF-R) was prepared as described earlier [14]. Pyrrole(Py), Acetonitrile, Dimethyl formamide, Acetone, and $NaClO_4$ 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. Potentiodynamic electrodeposition was performed with a Wenking POS 73 model potentiostat in conjugation with X-Y recorder (Kipp and Zonen).

In order to measure the electrical conductivity of the products, thin pellets were prepared by compacting the polymer powders under 10 tons of pressure. Typical sample diameter was 13 mm and the thickness was 0.8 mm. Conductivity measurements were performed by using Four-Probe Technique and calculated from the following equation:

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

where V is the potential in volts, I is the current in amperes, and dn is the thickness of the samples in cm.

A JEOL JSM T840 scanning electron microscope (SEM) was used for morphological studies.

Electrochemical Preparation of Py/MEKF-R Copolymer

The electrochemical synthesis of polymers was performed at a constant voltage of 1.2 V. Platinum electrodes were used as a counter- and a working-electrode and Ag wire as a reference. The polymerization solution consisted of acetonitrile containing pyrrole, resin, and 0.1 M of $NaClO_4$ as electrolyte. The films obtained on the surface of the working electrode were removed and washed with acetonitrile and dried at room temperature before characterization.

RESULTS AND DISCUSSION

Electrochemical Characterization

In order to investigate the pyrrole-resin interaction and the resulting product on the electrode surface current-potential curves of Py, MEKF-R and a mixture of Py/MEKF-R in acetonitrile and CV of coated electrodes were taken separately. Current-potential curves taken at a potential sweep rate of 20 mV/s are given in Figure 1. The measurements were carried out with ascending anodic potential. The curves (I), (II), and (III) concern current–potential curves

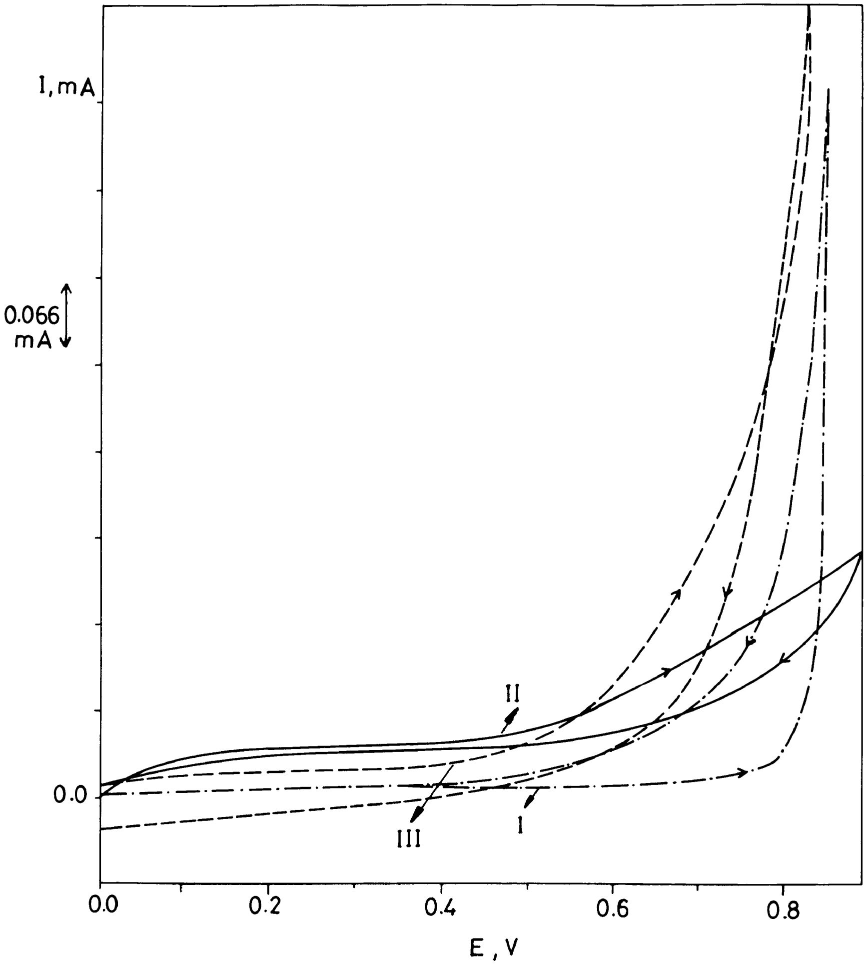

FIGURE 1 I-E curves of Pt electrodes in the presence of 0.01 M Py (I), 0.01 M MEKF-R (II), and mixture of Py and MEKF-R in the already described concentrations (III) in acetonitrile containing 0.1 M Sodiumpercholorate at a potential sweep rate of 20 mV/s.

(I-E curves) for electropolymerization of 0.01 M Py, 0.01 M MEKF-R, and the mixture of Py and MEKF-R at the same concentrations. The anodic current increased with the increase of anodic potential starting from 0.5 V (I), 0.4 V (II), and 0.45 V (III) for Py, MEKF-R, and Py/MEKF-R mixture, respectively. The curve (III) is regarded as a superposition of the curve (I) and the curve (II) indicating the inclusion of the resin in PPy on the surface of the working electrode.

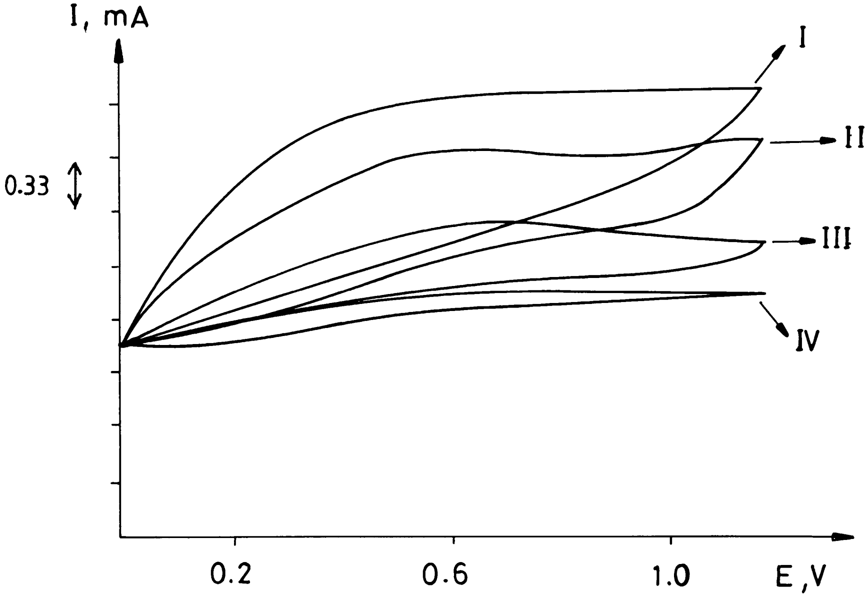

FIGURE 2 CV of coated electrodes in an acetonitrile solution containing 0.1 M Sodium percholorate at a potential sweep rate of 20 mV/s. I)-PPy, (II)-PPy in the presence of 0.01 M MEKF-R, (III)-PPy in the presence of 0.025 M MEKF-R, (IV)-PPy in the presence of 0.05 M MEKF-R.

For that reason, the CV of the coated electrodes were taken between 0.0 and 1.2 V in fresh electrolyte at a scan rate of 20 mV/s Figure 2. Decreasing current value in the presence of the resin (nMEKF-R/nPy = 0.5, 1, and 2.5 for the curve II, III, and IV, respectively) comparing PPy homopolymer electrode (the curve I) supports the previous conclusion that the resin was incorporated in the resulting polymer coating.

Electrical Conductivity

Electrical conductivities were measured by using four-probe technique. It was found that the conductivity of electrochemically prepared PPy was about 1×10^{-2} S/cm whereas Py polymerized in the presence of MEKF-R changes with the mole ratio of $n_{\text{MEKF-R}}/n_{\text{Py}}$ as seen in Table 1. Because the conductivity of the resin is very low, the reason for decreasing conductivity of the resulting product is the presence of the resin in the PPy chain.

TABLE 1 Conductivity of PPy Formed in the Presence of MEKF-R

No.	Py (Mol/1)	MEKF-R (Mol/1)	$n_{MEKF\text{-}R}/n_{Py}$	Conductivity, (S/cm)
1	0.01	—	—	1.0×10^{-2}
2	0.01	2.5×10^{-4}	0.025	1.0×10^{-3}
3	0.01	2.5×10^{-3}	0.25	2.5×10^{-4}
4	0.01	5×10^{-3}	0.5	1.0×10^{-4}
5	0.01	0.01	1	2.0×10^{-5}
6	0.01	0.02	2	5.0×10^{-6}
7	—	0.01	—	1.0×10^{-7}

FT-IR Results

The FT-IR spectra of electrochemically prepared homopolymer PPy (I), electrochemically prepared PPy in the presence of MEKF-R (II), and MEKF-R after electrolsis at the same conditions (III) are shown in Figure 3. The copolymer of PPy/resin has different characteristics then homopolymer of Py and the MEKF-R separately (Figure 3, line II). The intensity of the C=O vibration peak at $1700\,\text{cm}^{-1}$ in the MEKF-R spectrum (Figure 3, line IV) decreases in the copolymer. In order to investigate the effect of electrochemical oxidation, MEKF-R was oxidized anodically at $+1.2\,\text{V}$. The FT-IR spectrum of the electro-oxidized resin at the same conditions of the copolymer formation is given in Figure 3, line III. Somehow, the carbonyl peak of the resin is almost absent in the spectrum.

Spectral Analysis

Spectroelectrochemical methods were also employed to study the changes in band position of the polymers during oxidation. Polymer films were electrochemically produced on ITO glass and subsequently washed with acetonitrile and placed in quartz quvette with counter- and reference-electrodes for spectroelectrochemical analysis. An example of such spectra obtained by in-situ measurements is given in Figure 4 where three peaks were observed at three different wavelengths which are $\pi \rightarrow \pi^*$ transition at 320 nm, polaron at 450 nm, and bipolaron at 850 nm for oxidized state of PPy. Lines I and VIII represent the first minute and after having applied the 1.2 V, 10 min. Figure 5 shows the polymerization of Py in the presence of MEKF-R at the same conditions. Lines I and VIII represent the first minute and 10th min while applying the 1.2 V. Because radical cations of Py oligomers may react with the resin radicals, the absence of peak at 450 nm in this spectrum can be explained by this interaction.

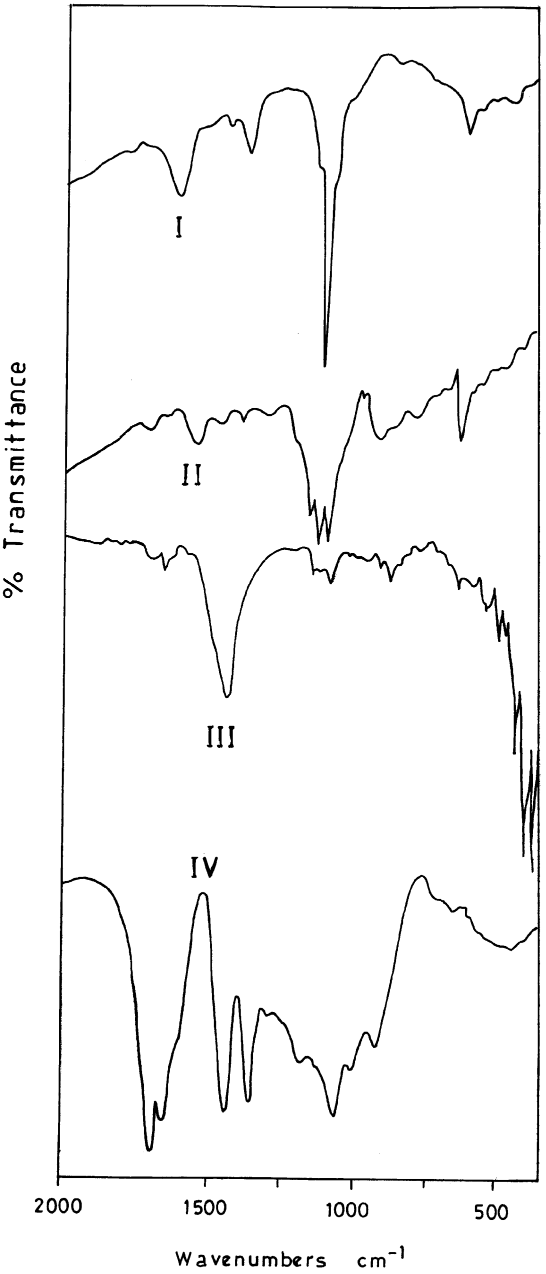

FIGURE 3 FT-IR spectra of electrochemically prepared PPy (I), and PPy in the presence of MEKF-R (nMEKF-R/nPy = 1) (II), MEKF-R after electrolyse at 3 V for 15 min (III), FT-IR spectra of MEKF-R alone (IV).

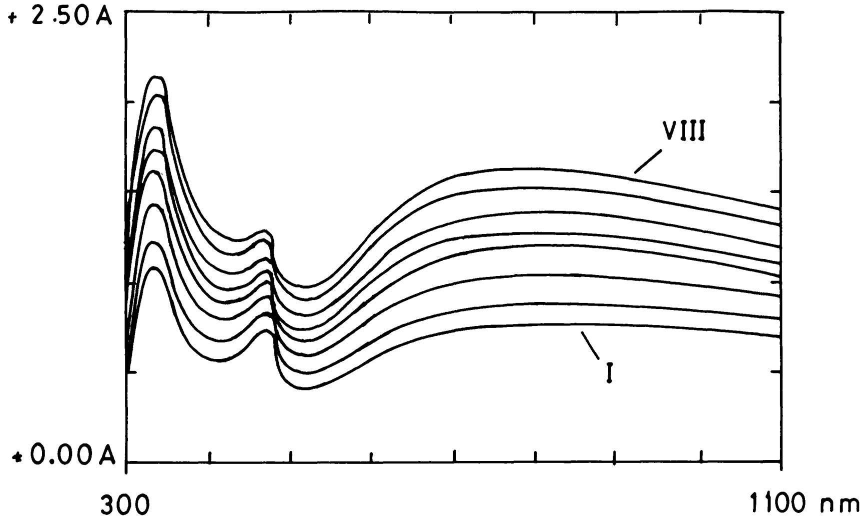

FIGURE 4 UV-Visible absorption spectra of PPy film on ITO electrode. (I)—obtained by oxidation at 1.2 V for 30 s. (VIII)—obtained by oxidation at 1.2 V for 10 min.

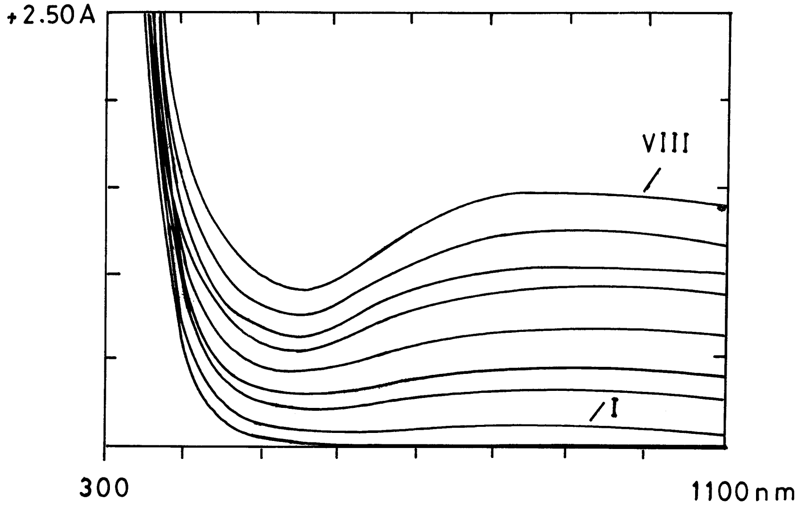

FIGURE 5 UV-Visible absorption spectra of PPy-MEKF-R copolymer film on ITO electrode. (I)—obtained by oxidation at 1.2 V for 30 s. (VIII)—obtained by oxidation at 1.2 V for 10 min.

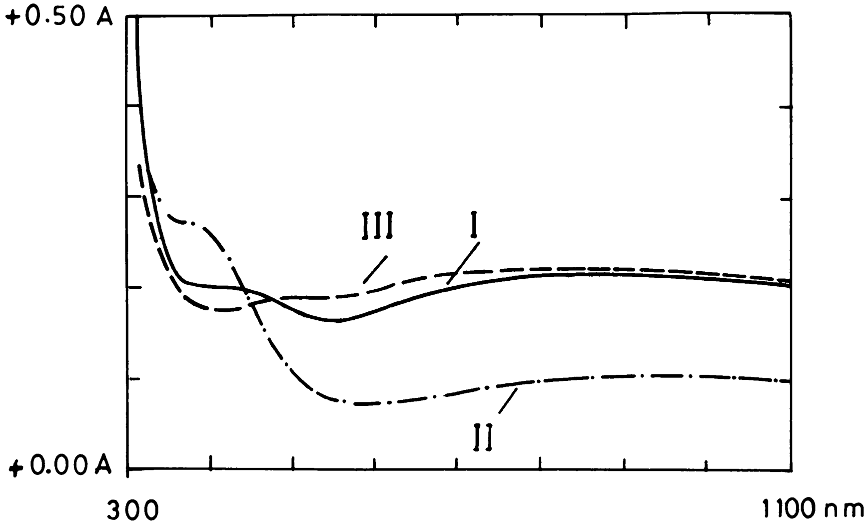

FIGURE 6 UV-Visible absorption spectra of oxidized (I), neutral that obtained by reduction at –1.2 V for 30 s. (II), and reoxidized at 1.2 V for 30 s. (III) PPy film on ITO electrode.

The spectrum of PPy film in the electrolyte is given in Figure 6. In order to investigate the switching properties of PPy between reduced and reoxidized states, the next experiment was done: First –1.2 V and then +1.2 V were applied to the neutral PPy film and the spectra for both cases, was obtained.

As the polymer was reduced at –1.2 V, the absorption peaks around 450 nm and 850 nm decrease, which is consistent with the disappearence of cationic charge carriers, whereas the peak at 320 nm increased. Reoxidation of the film results in a decrease in the absorption peak at 320 nm whereas a new broad peak beyond 700 nm appears. This is attributed to the reformation of delocalized cationic charge carriers. In the case of copolymer film, the spectra of reduced and reoxidized forms of Py-MEKF-R are given in Figure 7. Observed reversible electrochemical behavior of the copolymer film obtained at the mole ratio of $n_{\mathrm{MEKF\text{-}R}}/n_{\mathrm{Py}} = 1$ is found to be as good as the PPy film alone.

Morphological Analysis (SEM Results)

Representative SEM micrograph of the liquid side of the films prepared electrochemically form Py and MEKF-R mixture is shown in Figure 8. The SEM picture of PPy film (Figure 8a) shows clusters of

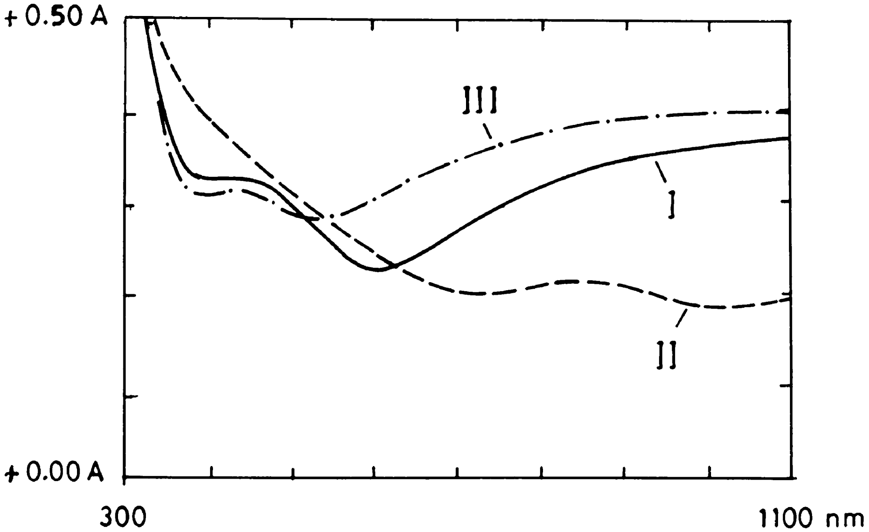

FIGURE 7 UV-Visible absorption spectra of oxidized (I), neutral that obtained by reduction at –1.2 V for 30 s. (II), and reoxidized at 1.2 V for 30 s. (III). Py-MEKF-R copolymer film on ITO electrode.

globules (approximate diameter of 4 μm) with void spaces in between, but in the SEM picture of the PPy formed in the presence of MEKF-R (Figure 8b), these spaces were filled and have more smooth surface. This may explain the better adhering property of the Py/MEKF-R copolymer.

Mechanism of Formation

All polymerization products are obtained as insoluble film, although the same concentrations of the resin and pyrrole had given soluble Py/MEKF-R copolymer in the chemical polymerization method [13]. This might be due to the electron transfer to Py monomer from the electrode through the copolymer film, which coated the electrode surface during the electropolymerization and resulted in overoxidized and crosslinked copolymer film. A possible mechanism of copolymer formation is shown in Scheme 1. This mechanism involves electrochemical polymerization reactions of Py and electrochemical reactions of MEKF-R.

A generally accepted initiation mechanism of the electropolymerization of Py is thought to be the formation of unstable Py radical cations at the anode surface [15], which can dimerize with the expulsion of

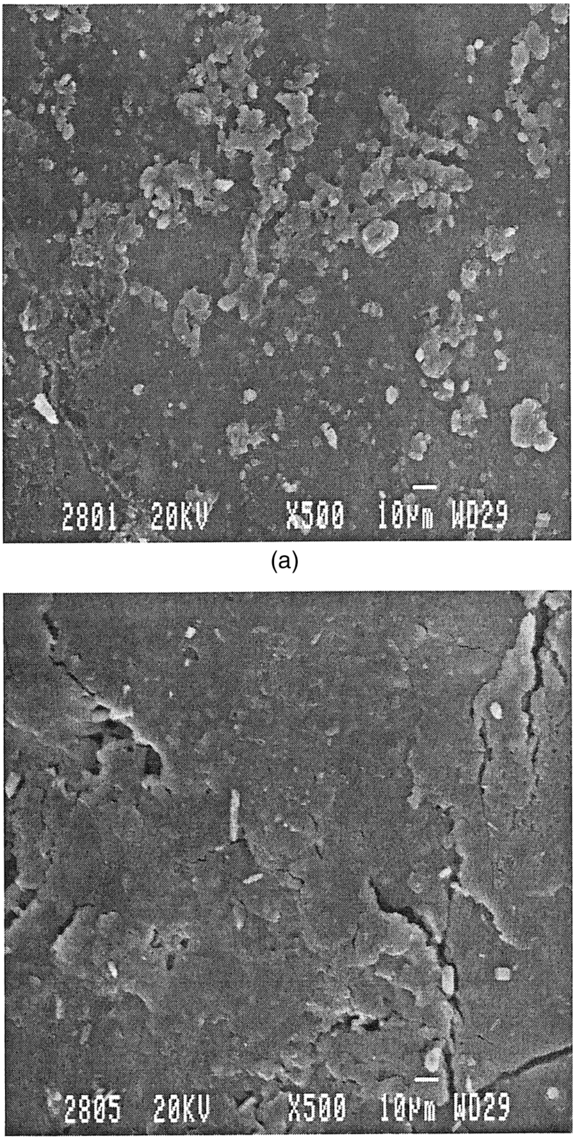

FIGURE 8 SEM micrographs of PPy (a), polymer film of Py in the presence of MEKF-R ($n_{\text{MEKF-R}}/n_{\text{Py}} = 1$) (b).

$2H^+$. Several steps follow the formation of oligomers, including the oxidation of oligomers by the removal of π electrons and H^+, forming tetramer radicals. Because the reactivity of tetramer radical would be lower than radical monomer [16], this tetramer radicals probably reacts first with the resin radicals to form initial Py/MEKF-R copolymer species. Typical chain growth mechanism takes place.

CONCLUSIONS

During the PPy formation on ITO electrode, which was followed by UV-Visible measurements, the maximum absorbance around 450 nm, attributable to the formation of polarons, disappeared in the presence of MEKF-R. This result supports the occurrence of a reaction between polarons and the radicals of MEKF-R. Even though the conductivity of the copolymer is lower than that of PPy, the switching property between oxidized and reduced forms of the copolymer films is not reduced. Insoluble products are probably due to crosslinking of the formed polymers by overoxidation. The formed smooth Py/MEKF-R copolymer films adhere to the surface of Pt electrode much better than PPy film produced under similar conditions. This property of the copolymer, beside reversible electrochemical behavior, might give some advantages during the application of conductive PPy. Furthermore, by changing the ratio of Py/MEKF-R, copolymers with conductivity in between PPy homopolymer and MEKF-R could be synthesized.

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