

# Soluble Polypyrrole Copolymers

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**ABSTRACT:** A new class of dimethyl formamide (DMF)- and acetone-soluble conducting pyrrole-ketonic resin copolymers has been developed. This was accomplished by oxidatively polymerizing pyrrole monomer by Ce(IV) salt in the presence of methyl ethyl ketone formaldehyde resin (MEKF-R). The resulting copolymers were readily dissolved in DMF and acetone. These products were characterized by FTIR and UV-visible spectroscopy, conductivity, four-probe conductivity, viscosity, and DSC measurements. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1098–1106, 2001

**Key words:** soluble polypyrroles; chemical polymerization; ketonic resin-pyrrole copolymers; ethyl methyl ketone-formaldehyde resin; conductive polymers

## INTRODUCTION

Electrically conducting polymers made from heterocyclic monomers have been the subject of much research in recent years. Polypyrrole (PPy) has received considerable interest, partly because it can be prepared both electrochemically<sup>1</sup> and by chemical oxidation<sup>2,3</sup> and partly because of its relatively good stability in the conducting, oxidized form. Despite its long history, the mechanism of pyrrole polymerization under oxidizing conditions has not been well understood because the polypyrroles are insoluble powders and cannot be characterized by conventional methods.<sup>4</sup>

The difficulty in solubility of conductive polypyrrole originates from its delocalized  $\pi$ -electronic structure, which is the very same molecular characteristic that gives rise to its novel optical and electronic properties necessary for applications. The delocalized  $\pi$ -electronic structure leads to large electronic polarizability and large interchain  $\pi$ - $\pi$  interaction, which favors aggregation instead of solution of polymer. It is possible to

decrease this polarizability by structural modification, although in this case the polymer would lose all of its useful optical and electronic properties.<sup>6</sup>

Polymers are introduced to the reaction media to overcome the solubility problem of PPy. However, these polymers belong to the class of neutral polymers that only exhibit physical adsorption of PPy, which is in the colloidal form.<sup>5</sup>

Another way to overcome the solubility problem of PPy to obtain polymer-polymer complexes, either by interaction of opposite charges of two macromolecules<sup>7</sup> or by matrix polymerization.<sup>8–10</sup> In the latter case the polymerization products have low conductivities ( $10^{-6}$  S/cm) because of very low conductivity of the matrix polymer (in the case of polyacrylic acid,  $10^{-8}$  S/cm).<sup>11</sup>

Conductive resins have been the subject of recent research. Conductive cyclohexanone-formaldehyde resins were prepared by an *in situ* modification technique<sup>12,13</sup> using a number of aldehydes such as glyoxal, benzaldehyde, and acetaldehyde as modifiers. Conductivity of the acetaldehyde-modified cyclohexanone-formaldehyde resin was  $10^{-3}$  S/cm.<sup>14</sup>

In this study the oxidative polymerization of pyrrole by ceric (IV) ammonium nitrate,<sup>3</sup> in the presence of methyl ethyl ketone-formaldehyde

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**Table I** Role of CAN Concentration on the Conductivity, Solubility, and the Yield of Copolymers<sup>a</sup>

Sample	[MEKF-R] ( $\times 10^{-3}$ )	[CAN]	Conductivity of Precipitate (S/cm)		Solubility <sup>b</sup> of Precipitate I		Yield (g)	
			I	II	DMF	Acetone	I	II
1	8.6	0.011	$2 \times 10^{-6}$	$2 \times 10^{-6}$	s	s	0.11	0.068
2	8.6	0.022	$7 \times 10^{-4}$	$3 \times 10^{-6}$	s	s	0.17	0.323
3	8.6	0.033	$2 \times 10^{-3}$	$5 \times 10^{-6}$	sl	sl	0.30	0.10
4	—	0.022	$2 \times 10^{-2}$	—	i	i	0.066	—
5	4.3	0.033	$4 \times 10^{-3}$	—	i	i	0.19	0.12

<sup>a</sup> [Py] = 0.058.<sup>b</sup> s = soluble; i = insoluble; sl = slightly soluble.

resin (MEKF-R) was investigated. The roles of MEKF-R, pyrrole, and Ce(IV) concentration, the order of component addition into the polymerization system on the yield, and the conductivity of the product were investigated.

## EXPERIMENTAL

### Materials

Methyl ethyl ketone-formaldehyde resin (MEKF-R), prepared as previously described,<sup>15</sup> had a molecular weight of about 700 g/mol. Pyrrole (Py), acetonitrile, dimethyl formamide (DMF), acetone (Ac), and ceric ammonium nitrate ( $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  (CAN) were all reagent-grade chemicals (Merck, Darmstadt, Germany) 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.

DSC thermograms were obtained with a Perkin-Elmer DSC-6 instrument (Perkin-Elmer, Palo Alto, CA), at a heating rate of 10°C/min under nitrogen atmosphere.

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

Viscometric data were collected using an Ostwald viscometer at 25°C.

### Preparation of Methyl Ethyl Ketone-Formaldehyde Resin-Polypyrrole Copolymers

First, the ketonic resin, CAN, and Py were separately dissolved in acetonitrile. The CAN solution

was then added to the resin solution dropwise under stirring. The color of the solution changed from pale yellow to reddish color. Finally, the pyrrole solution was added to the mixture. A black powder formed almost instantaneously. After 1 h, the precipitate was filtered, washed with acetonitrile several times, and dried at room temperature. This precipitate was called precipitate I and the precipitate obtained by pouring the filtrate into water was called precipitate II. Polymerization experiments were carried out at 25°C while stirring with a magnetic stirrer. The reaction volume was about 60 mL in all experiments.

### Conductivity Measurements

To measure the electrical conductivity of precipitates I and II, thin pellets were prepared by compacting the polymer powders under 10 tons of pressure. Typical sample diameters were 13 mm at a thickness of 0.8 mm. Conductivity measurements were performed by using the four-probe technique and calculated from the following equation:

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

where  $V$  is the potential in volts,  $I$  is the current in amperes, and  $d_n$  is the thickness of the samples in centimeters.

## RESULTS AND DISCUSSION

Solid-state conductivities of the polymers at room temperature are listed in Tables I, II, and III, according to the effect of CAN, Py, and MEKF-R concentrations, respectively.

The conductivity of PPy (sample 4) obtained chemically by Ce(IV) salt in acetonitrile is in the

**Table II** Role of Py Concentration on the Solubility, Conductivity, and Yield of Copolymers<sup>a</sup>

Sample	[Py]	Conductivity of Precipitate (S/cm)		Solubility <sup>b</sup> of Precipitate I	
		I	II	DMF (mg/100 ml)	Acetone
6	0.029	$7.0 \times 10^{-5}$	$1.5 \times 10^{-6}$	12	s
2	0.058	$7.0 \times 10^{-4}$	$3.0 \times 10^{-6}$	4	s
7	0.116	$1.3 \times 10^{-3}$	$4.0 \times 10^{-6}$	2	s
8 <sup>c</sup>	2.24	$1.0 \times 10^{-1}$	—	i	i
9	2.24	$2.8 \times 10^{-3}$	—	i	i

<sup>a</sup> [MEKF-R] =  $8.6 \times 10^{-3}M$ ; [CAN] = 0.222M.

<sup>b</sup> s = soluble; i = insoluble.

<sup>c</sup> In the absence of MEKF-Resin.

range observed in the literature.<sup>16</sup> The conductivity of soluble copolymer (sample 7) is also high enough ( $1.3 \times 10^{-3}$  S/cm), if it is compared with the conductivity of insoluble PPy ( $3.9 \times 10^{-2}$  S/cm) obtained in the acetonitrile/water mixture.

#### Role of Ceric Ammonium Nitrate (CAN) Concentration

The role of CAN concentration on the solubility and conductivity of copolymers was investigated at a constant ratio of  $n_{\text{MEKF-R}}/n_{\text{Py}} = 0.14$  by varying the CAN concentration from 0.011 to 0.0328M. Conductivity values and solubility properties of both precipitates I and II are presented in Table I.

The conductivity increases by increasing the CAN concentration. In the case of PPy obtained by Ce(IV) in the absence of MEKF-R (sample 4) the conductivity of insoluble product is the highest, as expected. It is interesting that the conductivity of precipitate II increases slightly by increasing the CAN concentration. Because MEKF-Resin has very low conductivity ( $2 \times 10^{-6}$  S/cm), these findings show the high MEKF-R inclusion to the PPy chain in precipitate II. The amount of precipitate I increases by increasing the CAN concentration. The lowest yield was obtained when MEKF-R was not used (sample 4) in this series, indicating that precipitate I in samples 1, 2, 3, and 5 contains MEKF-R, which makes the products soluble if a suitable MEKF-R/CAN/Py mol ratio is selected.

An increase in CAN concentration increases the yield of precipitate I (samples 1–3). However, if half the amount of MEKF-R concentration is used, the yield of precipitate I decreases even if the CAN concentration is held constant (see samples 3 and 5).

#### Role of Py Concentration

The effect of Py concentration on the yields, conductivity, and solubility was examined for different concentrations of Py, keeping the concentration of MEKF-R and CAN constant (Table II). Conductivity values of precipitate I increase by increasing Py concentration.

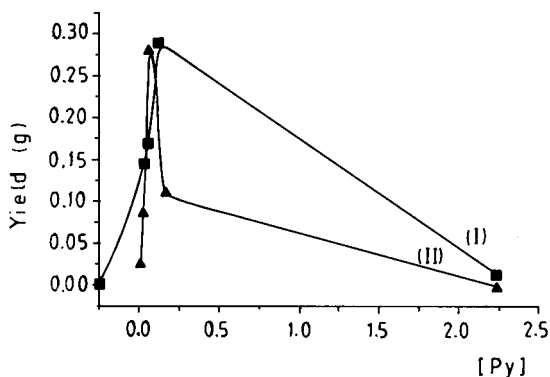
Experimental samples 8 and 9 show that, if the Py concentration is too high (2.24M), the copolymer becomes insoluble in DMF and acetone, indicating a long PPy chain in the copolymer structure. It is necessary to limit the  $n_{\text{MEKF-R}}/n_{\text{Py}}$  mol ratio to obtain a soluble copolymer. These results are parallel with increasing conductivities of precipitate I (Table II).

The conductivities of precipitate II are not affected significantly by Py concentration. Only a slight increase in conductivity is observed as in the case of precipitate II in Table I. This also supports the idea that precipitate I has high PPy content, whereas precipitate II has high MEKF-R content.

The relationship between the pyrrole concentration and the yield of precipitates I and II is given in Figure 1. Yields increase by increasing Py concentration up to 0.0116M, after which value they decrease. This shows that a high Py concentration decreases the possibility of MEKF-R inclusion into the PPy chain in the reaction mixture.

#### Role of Pyrrole Concentration on the Conductivities of Solutions

To support the solid conductivity results of both precipitates I and II, the next conductimetric measurements were done in solutions that were obtained by separately dissolving precipitates I

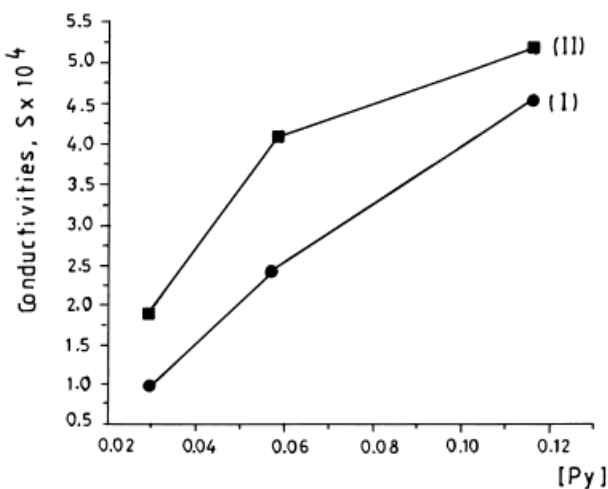


**Figure 1** Effect of pyrrole concentration on the solubility of precipitate I in DMF.

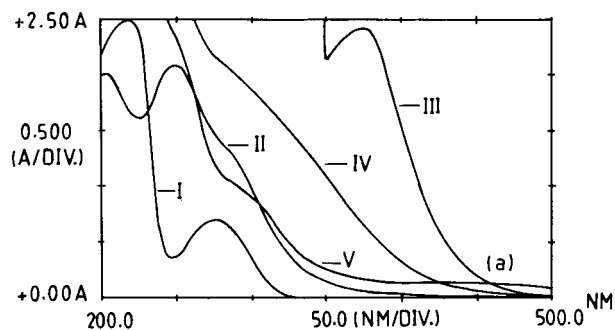
and II in DMF. The relationship between solution conductivities and Py concentrations is given in Figure 2. The conductivities of precipitates I and II increase by increasing the Py concentration (Fig. 2, lines I and II, respectively).

#### Spectral Analyses of MEKF-R-CAN-Py System

The copolymerization reaction of pyrrole and MEKF-R with Ce(IV) was investigated by following the absorption of soluble oxidized product. An example of such absorbance measurements is given in Figure 3. The shift in the absorbance of CAN (line III), compared against that of the MEKF-R-CAN mixture (line IV), indicates the interaction of MEKF-R with Ce(IV). Because the MEKF-R, Py, and Ce(IV) alone do not have any



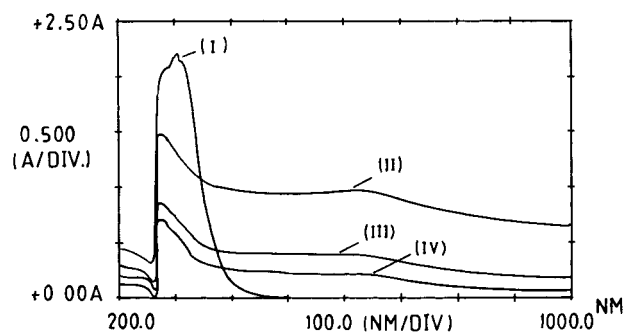
**Figure 2** Effect of pyrrole concentration on the conductivities of precipitate I in DMF(I) and precipitate II in DMF(II).



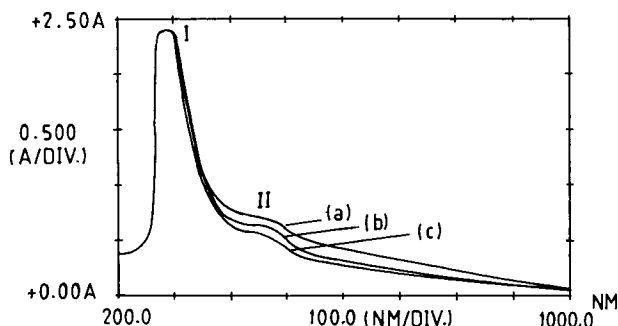
**Figure 3** Absorbance spectra of MEKF-R(I), Py(II), CAN(III), and the mixtures of MEKF-R-CAN(IV) and MEKF-R-CAN-Py(V). [MEKF-R] =  $8.6 \times 10^{-3} M$ , [CAN] = 0.022M, [Py] = 0.058M. (Diluted solutions by 1/20.)

absorbance at 450 nm (lines I, II, and III), the small peak at 450 nm [peak (a) on line V] may be attributed to the oligomeric products of the reaction.<sup>8</sup>

The relationship of the UV-visible spectrum of precipitate I of copolymers in DMF and the Py concentration is shown in Figure 4. All copolymer solutions have an absorbance at 275 and 650 nm, attributed to the MEKF-R and copolymerization products of Py with MEKF-R, respectively. Because MEKF-R alone gives the absorbance at 275 nm (Fig. 4, peak I), the decrease in the absorbance at 275 nm (Fig. 4, lines I-IV) can be explained by the decreasing MEKF-R content of the copolymers. On the other hand, decreasing the absorbance at 650 nm indicates the decreasing solubility of the copolymers. These also support our conclusion that, at higher Py concentration, the copolymer will have a longer PPy chain with less MEKF-R inclusion, which makes it insoluble.



**Figure 4** Absorbance spectra of MEKF-R alone (I), and the MEKF-R-CAN-Py mixtures: [Py] = 0.029M (II); [Py] = 0.058M (III); [Py] = 0.116M; [MEKF-R] =  $8.6 \times 10^{-3} M$ ; [CAN] = 0.022M.



**Figure 5** Absorbance spectra of precipitate II in DMF. (a)  $[Py] = 0.029M$ , (b)  $[Py] = 0.058M$ , (c)  $[Py] = 0.116M$ .  $[MEKF-R] = 8.6 \times 10^{-3} M$ ,  $[CAN] = 0.222M$ .

### Conductivity Results of Precipitate II

Figure 5 shows the UV-visible absorbance spectra of the solutions obtained by dissolving precipitate II of samples 6, 2, and 7 in DMF.

The absorbance of Py oligomers does not seem to be greatly affected by Py concentration because the high MEKF-R inclusion of copolymer is seen by observing the same absorbance value at 350 nm for all cases (Fig. 5, peak I). Small differences of peak II at 450 nm might be the result of rather small pyrrole oligomers with different sizes bonded to the ketonic resin at different Py concentrations [Fig. 5, lines (a)–(c), peak II]. These findings support the four-probe conductivity results of precipitate II, which are quite similar for all cases (Tables I and II).

### Role of MEKF-Resin Concentration

As can be seen from Table III, conductivities of precipitate I increase up to  $1.1 \times 10^{-2}$  from  $7.0 \times 10^{-4}$  S/cm if MEKF-R concentration is decreased from  $8.6 \times 10^{-3} M$  to  $7.8 \times 10^{-4} M$ .

Because samples 10 and 11 are insoluble in DMF and acetone,  $8.6 \times 10^{-3} M$  seems to be the concentration limit of MEKF-R to obtain soluble copolymers when the  $n_{CAN}/n_{Py}$  mol ratio is 0.38.

### Role of Addition Order of Components

To investigate the addition order of components the next experiment was carried out in the MEKF-R-Py-CAN order instead of MEKF-R-CAN-Py order. The resulting conductivities were  $2.8 \times 10^{-2}$  and  $2.8 \times 10^{-3}$  S/cm, respectively. These findings support the conclusion that the MEKF-R radical can be produced in the reaction medium at the beginning of the polymerization process, given that MEKF-R and Ce(IV) are mixed first and then Py is added to the mixture. If not, as in the case of the MEKF-R-Py-CAN order, MEKF-R could find less chance to react with CAN so that the MEKF-R inclusion into the PPy chain would be low, thus resulting in the higher conductivity of PPy-MEKF-R copolymers.

### FTIR Spectra

FTIR spectra of chemically prepared PPy by Ce(IV), PPy-MEKF-R copolymer (precipitates I and II) are shown in Figure 6.

The FTIR spectrum of copolymer (precipitates I and II) indicates Ce(III) and  $NO_3^-$  ligands incorporated into the polymer [Fig. 6, lines (b) and (c),  $\gamma = 1384 \text{ cm}^{-1}$ ]. Similar incorporation of Ce(III) and  $NO_3^-$  ligand into PPy can be observed in PPy homopolymer [line (a)].

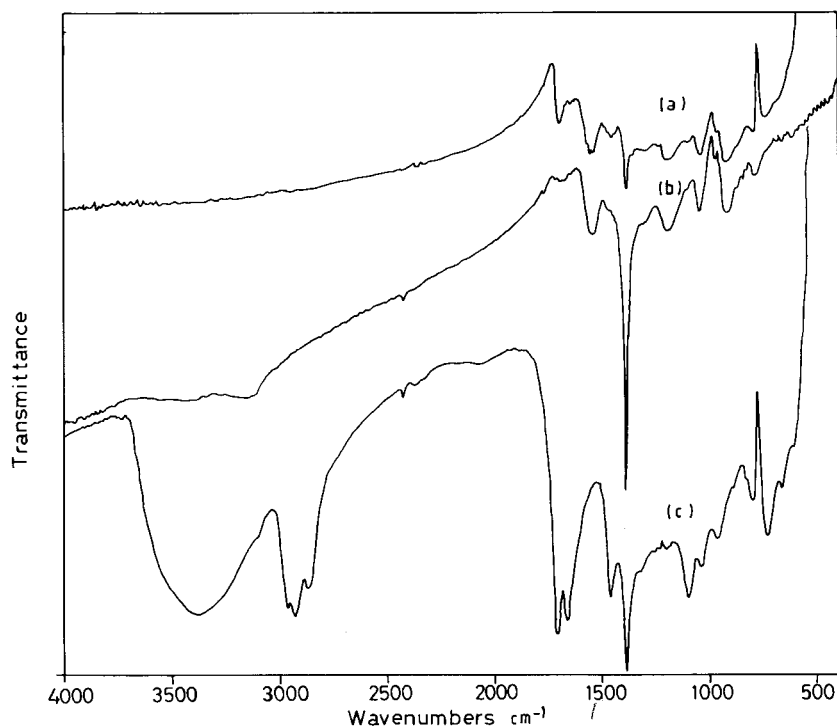
It must be noted that, although the spectrum of precipitate I of sample 1 [line (b)] is similar to that of the PPy spectrum [line (a)] with characteristic peaks for stretching vibration of Py ring and aromatic C-H vibration at 1542 and 925  $\text{cm}^{-1}$ , respectively, the spectrum of precipitate II

**Table III** Role of MEKF-R Concentration on the Solubility, Conductivity, and Yield of Copolymers<sup>a</sup>

Sample	[MEKF-R]	Conductivity of Precipitate (S/cm)		Solubility <sup>b</sup> of Precipitate I		Yield (g)	
		I	II	DMF	Acetone	I	II
2	$8.6 \times 10^{-3}$	$7.0 \times 10^{-4}$	$3.0 \times 10^{-6}$	s	s	0.146	0.098
10	$4.3 \times 10^{-3}$	$1.2 \times 10^{-3}$	—	i	i	0.170	0.323
11	$7.8 \times 10^{-4}$	$1.1 \times 10^{-2}$	—	i	i	0.290	0.124

<sup>a</sup>  $[CAN] = 0.222M$ ;  $[Py] = 0.058M$ .

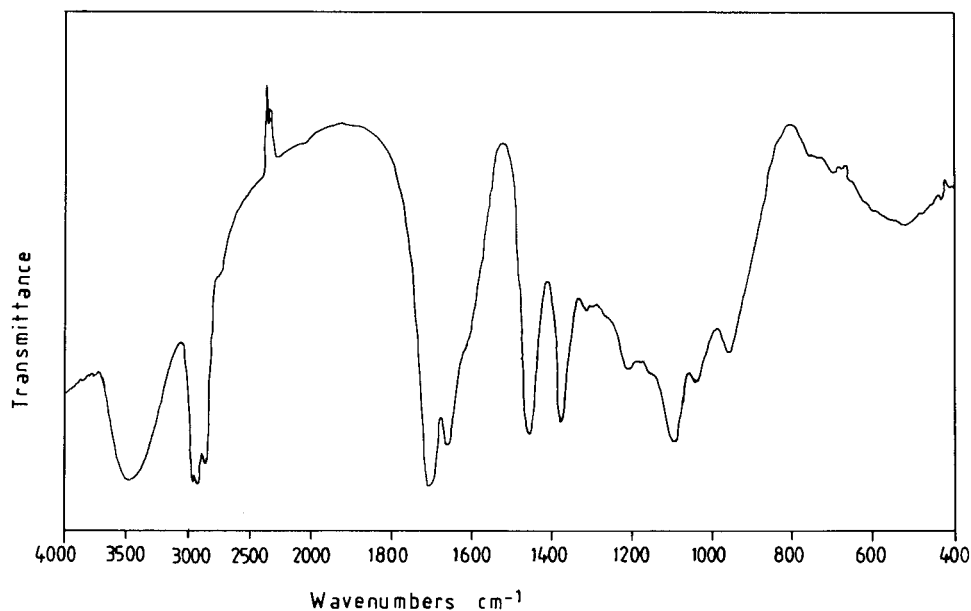
<sup>b</sup> s = soluble; i = insoluble.



**Figure 6** FTIR spectra of chemically prepared PPy by (a) Ce(IV), (b) PPy-MEKF-R copolymer (sample 2, precipitate I), (c) PPy-MEKF-R copolymer (sample 2, precipitate II).

of the same experiment [line (c)] is similar to that of the MEKF-R spectrum (Fig. 7) with a characteristic peak for  $\text{C}=\text{O}$  stretching and aliphatic

$\text{C}-\text{H}$  stretching at  $1680$  and  $2930\text{ cm}^{-1}$ , respectively. These findings support the conclusion that the copolymer (precipitate II) consists of a poly-



**Figure 7** FTIR spectrum of MEKF-R alone.

pyrrole chain that is long enough to have very similar conductivities to those of pure PPy (see Tables I–III). Decreases in the solid-state conductivities and very similar spectra of precipitate II with MEKF–R are most probably the result of the termination by MEKF–R radicals resulting from MEKF–R–PPy copolymers. This MEKF–R inclusion into the PPy chain can explain the solubility of resulting copolymers in DMF and acetone.

### Viscosity Measurements

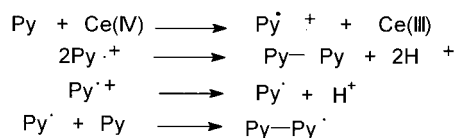
To understand the effect of pyrrole concentration on the chain length of copolymer, the viscosity of solutions obtained by dissolving precipitate I of samples 6, 2, and 7 in DMF were measured, the results of which are presented in Table IV.

**Table IV** Viscosity Values of Py–MEKF–R Copolymers

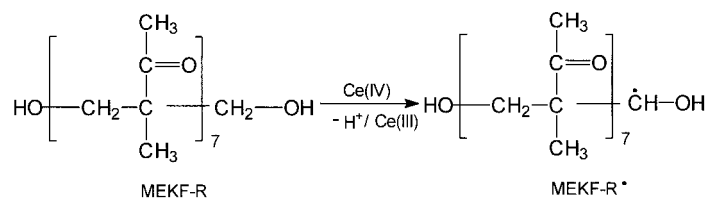
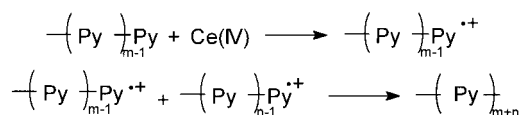
Sample	[Py]	$\eta_{sp}/c$ (dL/g)	
		Precipitate I	Precipitate II
6	0.029	12.2	0.40
2	0.058	52.1	0.40
7	0.116	135.4	0.40

Given that MEKF–R viscosity alone in DMF was 0.40 dL/g, the same viscosity values of precipitate II for three samples indicates that they consist almost solely of MEKF–R resin. Similar FTIR spectra of MEKF–R and precipitate II and conductivity results also support this conclusion. [See Fig. 6, line (c), and Fig. 7.]

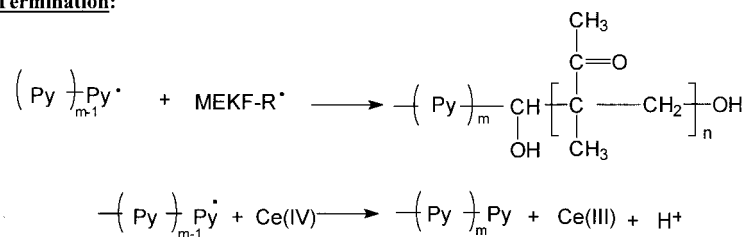
#### Initiation:



#### Propogation



#### Termination:



**Scheme 1**

Viscosities of precipitate I increase by increasing the Py concentration, which is probably attributed to the growing, longer PPy chain.

### Thermal Analysis

The DSC scan of PPy shows no glass-transition temperature ( $T_g$ ), which is a characteristic property of conducting polymers. Because MEKF-R has a  $T_g$  at 145°C, it is not surprising to observe  $T_g$  at 150 and 165°C for precipitate II of samples 7 and 3, respectively. Because they are almost solely MEKF-R, precipitate I of samples 7 and 3 have no  $T_g$ , as expected, because of their higher PPy content.

### Mechanism

The initial step in the electropolymerization of pyrrole is thought to be formation of unstable pyrrole radical cations at the anode surface.<sup>16</sup> Polymerization in solution can also proceed by oxidation of Py by Ce(IV) to form radical cations (Py<sup>•+</sup>), which can dimerize with the expulsion of H<sup>+</sup> in the proposed mechanism for electrochemical synthesis<sup>17</sup> (see Scheme 1).

The second mechanistic possibility in the initiation step is the proton loss of radical cation and radical attached onto a natural monomer molecule.<sup>18</sup>

In the propagation step, polymer chains continue to grow as long as pyrrole and Ce(IV) are available.

Formation of MEKF-R radical by Ce(IV) was proposed as previously reported.<sup>19</sup>

In contrast to the matrix polymerization of Py, by changing the order of addition to MEKF-R, CAN, and Py, MEKF-R can find time to interact with Ce(IV) first. Thus MEKF-R radicals and Ce(III)-MEKF-R complexes are always present in the polymerization media.

Because PPy may interact with the Ce(III)-MEKF-R complex, it is not possible to describe a complete structure of copolymerization products.

In the termination step, growing PPy radicals may combine with MEKF-R radicals to produce PPy-MEKF-R copolymers.

Termination of the growing PPy chain by Ce(IV) is also possible.

### CONCLUSIONS

MEKF-R-PPy copolymers prepared chemically by Ce(IV) in acetonitrile exhibit differences in

their morphologies; however, the presence of aromatic C—H vibrations from PPy and the characteristic peak for C=O stretching and aliphatic C—H stretching from MEKF-R are evident for copolymerization, as shown by infrared spectroscopy.

The results presented in this study show that the solubilities and conductivities of the products depend on the MEKF-R/Ce(IV)/Py ratio. The limit of mol ratios to obtain both soluble and conductive copolymer of Py and MEKF-R by Ce(IV) in acetonitrile was found to be  $n_{\text{CAN}}/n_{\text{Py}} = 0.19$  and  $n_{\text{MEKF-R}}/n_{\text{CAN}} = 0.39$  (Table II, sample 7).

Consequently, if the MEKF-R/Ce(IV)/Py ratio is suitably selected, fairly conductive and soluble PPy-MEKF-R copolymers could be synthesized in nonaqueous solvent. This means that one can overcome the solubility problem of PPy and use conventional methods for characterization. By the advantage of obtaining soluble polypyrrole-MEKF-R copolymers, a combination of several methods such as UV-visible spectroscopy, conductometry, and viscosimetry gives the possibility of investigating the formation of copolymer in detail. Besides, producing soluble PPy copolymers will overcome the application difficulties resulting from the insolubility of PPy and open new application areas such as antistatic surface coatings.

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