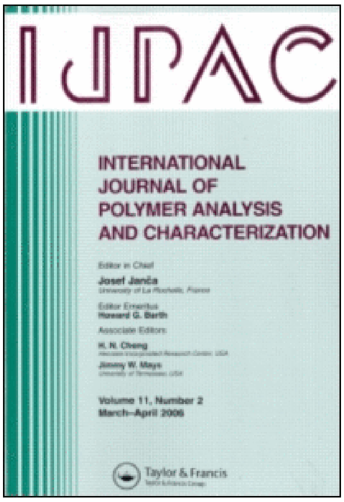

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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Belkis Ustamehmetoğlu[a]; Eda Kelleboz[a]; A. Sezai Sar[a]
[a] Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, Istanbul, Turkey

To cite this Article Ustamehmetoğlu, Belkis , Kelleboz, Eda and Sar, A. Sezai(2003) 'Oxidative Copolymerization of Pyrrole and N-Methyl Pyrrole', International Journal of Polymer Analysis and Characterization, 8: 4, 255 — 268
To link to this Article: DOI: 10.1080/10236660304882
URL: http://dx.doi.org/10.1080/10236660304882

International Journal of Polymer Anal. Charact., 8: 255–268, 2003
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ISSN: 1023-666X print
DOI: 10.1080/10236660390198448

Oxidative Copolymerization of Pyrrole and N-*Methyl Pyrrole*

Belkis Ustamehmetoğlu, Eda Kelleboz, A. Sezai Saraç
Department of Chemistry, Faculty of Science and
Letters, Istanbul Technical University, Istanbul, Turkey

Pyrrole and N-*methyl pyrrole were copolymerized by ceric ammonium nitrate (CAN) in aqueous solution. The resulting products were characterized by Fourier-transform infrared spectroscopy, UV-visible spectroscopy, and four-point probe conductivity measurements. The specific electrical conductivity of the copolymers can be increased depending on the mole ratio of pyrrole/*N-*methylpyrrole. The conductivities of copolymers are in the range of* 10^{-4}–10^{-2} $S\,cm^{-1}$. *Kinetic parameters were obtained by gravimetric determination of the copolymer and found to be dependent on* $[pyrrole]^{0.87}$ $[N\text{-}methyl\ pyrrole]^{0.06}$ $[CAN]^{0.11}$ $[H_2SO_4]^{1.28}$ *from gravimetric determination.*

Keywords: Chemical polymerization; Copolymerization of pyrrole and *N*-methyl pyrrole; Ceric salt

INTRODUCTION

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[1,2]. Attempts have been made in the copolymerization of pyrrole (Py) with other heterocyclic monomers

Accepted 28 January 2002.

Address correspondence to Belkis Ustamehmetoğlu and A. Sezai Saraç, Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey. E-mail: sarac@itu.edu.tr

to improve the properties of the resulting product. The copolymer is expected to gain both conductivity and good mechanical properties from its two components[3]. So far, Py and *N*-methyl pyrrole[4], Py and phenol[5], Py and terthienyl[6], Py and tetralkyl ammonium[7], and Py and acrylamide[8] have been prepared by electrolytic oxidation of the mixture of monomers. Good quality PPy films were obtained[9] and measurements on *N*-substituted polyprroles were performed[10,11]. The introduction of an *N*-substituent results, as a rule, in a decrease in electronic conductivity of the polymer; the redox potential of the polymeric electrode is, however, significantly increased[10]. Naoi et al.[12] followed this concept and investigated poly(*N*-methyl pyrrole) films in lithium cells. Although some reports have appeared on the halogen-induced chemical copolymerization of pyrrole with *N*-methyl pyrrole[13], the chemical copolymerization of pyrrole and *N*-methyl pyrrole has not been investigated in detail, even though it is more convenient and economical. Several investigations have been performed to observe the effect of various parameters on the structural morphology, dielectric relaxation behavior, electrical conduction, and mechanism of charge transport of the pyrrole and *N*-methyl pyrrole obtained by electrochemical copolymerization[14–17].

To extend our knowledge about pyrrole–*N*-methyl pyrrole random copolymer, in this study the chemical polymerization of two monomers was investigated in detail with the aim of obtaining a copolymer having better physical and conductivity properties than corresponding co-monomers.

EXPERIMENTAL

Materials

Ceric ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$ (CAN), pyrrole, *N*-methyl pyrrole, sulfuric acid, and acetonitrile (ACN) were all Merck reagent-grade chemicals of the highest purity and were used without further purification.

Polymerization Procedure

Pyrrole and *N*-methyl pyrrole and cerium (IV) salt were dissolved separately in water in the presence of H_2SO_4. CAN solution was slowly added to the mixture of monomer solutions, which were being continuously stirred during the polymerization process. A black powder formed almost instantaneously . The black powder was thoroughly and repeatedly washed with water until the filtrate was colorless. The powder was then dried at room temperature.The copolymer yield was determined by direct weighing of the polymerization products.

Polymer Characterization

Infrared (IR) spectra were recorded on a Matson 1000 Fourier-transform infrared spectrometer using KBr pellets. All reactions were monitored between 200 and 1100 nm by using a UV-visible spectrophotometer (Shimadzu 160 A). Electrical conductivities of the solid products were measured from pellets by using the four-point probe technique.

The kinetic measurements were done as follows. First, the polymerization rate (Rp) values were obtained from the slopes of the weight-time curves for different concentrations of Py, *N*-methyl pyrrole, CAN, and H_2SO_4. A logarithmic representation of the Rp against log(monomer), log(CAN), and log(H_2SO_4) separately gave a straight line whose slope is order dependent. In this way an order dependence on the monomers, CAN, and H_2SO_4 may be obtained.

RESULTS AND DISCUSSION

Effect of CAN Concentration

The yield of copolymerization of pyrrole and *N*-methyl pyrrole was studied by varying the concentration of CAN from 0.015 to 0.1 M. The results show that increasing the CAN concentration increases the yield. Since the solubility of CAN is limited to low concentrations, 0.05 M CAN was chosen for the experiments.

Effect of Solvent

The effect of solvent on the copolymerization yield was investigated and results were collected in Table I.

TABLE I The effect of solvent on the copolymerization yield

Pyrrole (M)	*N*-Methyl pyrrole (M)	Solvent	Yield (g)
0.035	0.035	H_2O	0.019
0.035	0.035	ACN/ H_2O	0.015
0.035	0.035	ACN	0.013
0.07	—	ACN/ H_2O	0.015
—	0.07	ACN/ H_2O	0.014
0.035	0.035	0.05 MH_2SO_4	0.039

Ce(IV) = 0.01 M.

The data in Table I show that 0.05 M H_2SO_4 is a suitable medium for this copolymerization and was used for all experiments.

Spectral Analyses

FTIR Spectra

The FTIR spectra of the copolymer (mole ratio: $n_{Py}/n_{NMPy} = 1{:}1$)(I), chemically sythesized PPy(II), and chemically synthesized poly (*N*-methyl pyrrole) P(N-MPy)(III) are shown in Figure 1. The peak at 1380 cm^{-1}indicates the cooperation of cerium(III) nitrate and/or nitrate into the polymer.

Both N-H bending vibration and stretching vibration of the pyrrole ring have a characteristic band at about 1620 cm^{-1}(II). Due to the overlapping of these characteristic peaks of PPy and P(N-MPy), a change at about 1700 cm^{-1}, which is the $C=O$ peak of the pyrrolidone structure, occurs by overoxidation of the pyrrole ring by strong oxidants. The actual mechanism of overoxidation in polypyrrole has been considered in some detail by Christensen et al.[18]. Note that oxygen is introduced from water present in the reaction medium. Because the overoxidation tendency of *N*-methyl pyrrole occurs using the same amount of cerium salt, as compared to pyrrole. The next experiment was carried out in different concentrations of CAN (Figure 2) to investigate the effect of CAN concentration on the overoxidation in the case of *N*-methyl pyrrole. As can be seen from Figure 2, as we move from 0.05 M to 0.15 M CAN, the $C=O$ peak of pyrrolidone structure, which is the result of over oxidation, appears at 1716 cm^{-1} (Figure 2, spectrum II), showing the inclusion of *N*-methyl pyrrole into the PPy structure.

To show the relation of the peak at 1716 cm^{-1} attributed to over oxidation and *N*-methyl pyrrole presence in the copolymer structure, the next experiment was carried out with a different concentration of pyrrole and *N*-methyl pyrrole (Figures 3 and 4). In the pyrrole case, there is no carbonyl peak (Figure 3), indicating absence of the pyrrolidone structure in the PPy chain due to the overoxidation. As can be seen from Figure 4, the $C=O$ peak at 1716 cm^{-1} appears after the second spectrum (Figure 4, spectrum II), which has sufficient *N*-methyl pyrrole inclusion into the PPy chain to be oxidized and form a pyrrolidone structure.

UV-Visible Spectra

The copolymerization reaction of pyrrole and *N*-methyl pyrrole by Ce(IV) salt was investigated by following the absorbtion of the mother-liquors of the polymerization products. An example of such absorbance measurements is given in Figure 5, where three peaks were observed generally at two different wavelengths, i.e., 300 nm(I) and 450 nm(II).

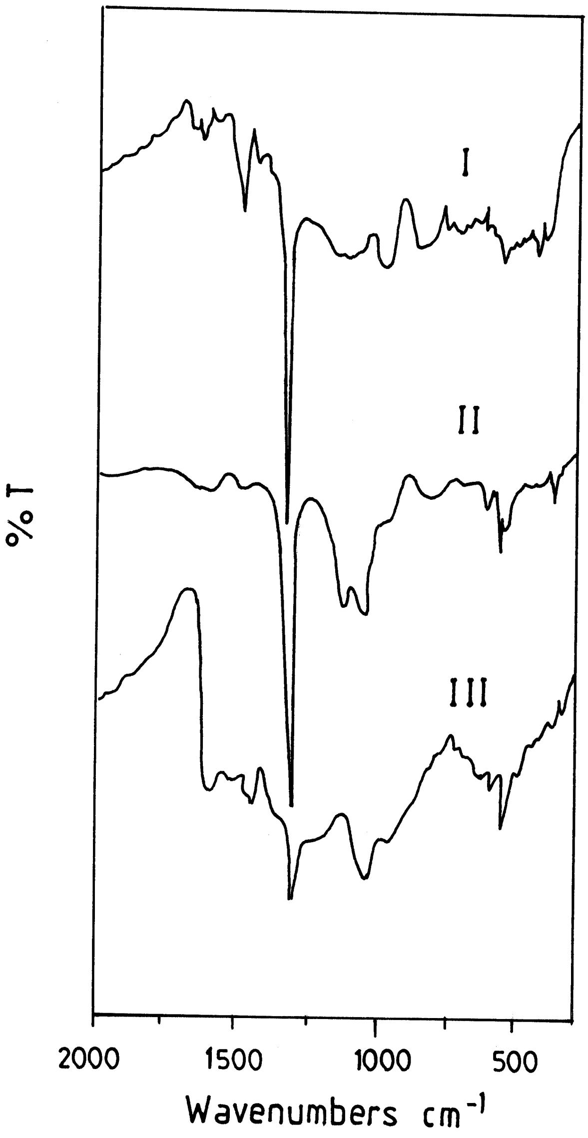

FIGURE 1 FTIR spectra of copolymer $(n_{Py}/n_{NMPy}) = 1{:}1$ (I), chemically synthesized PPy (II), and chemically sythesized *N*-methyl pyrrole (III).

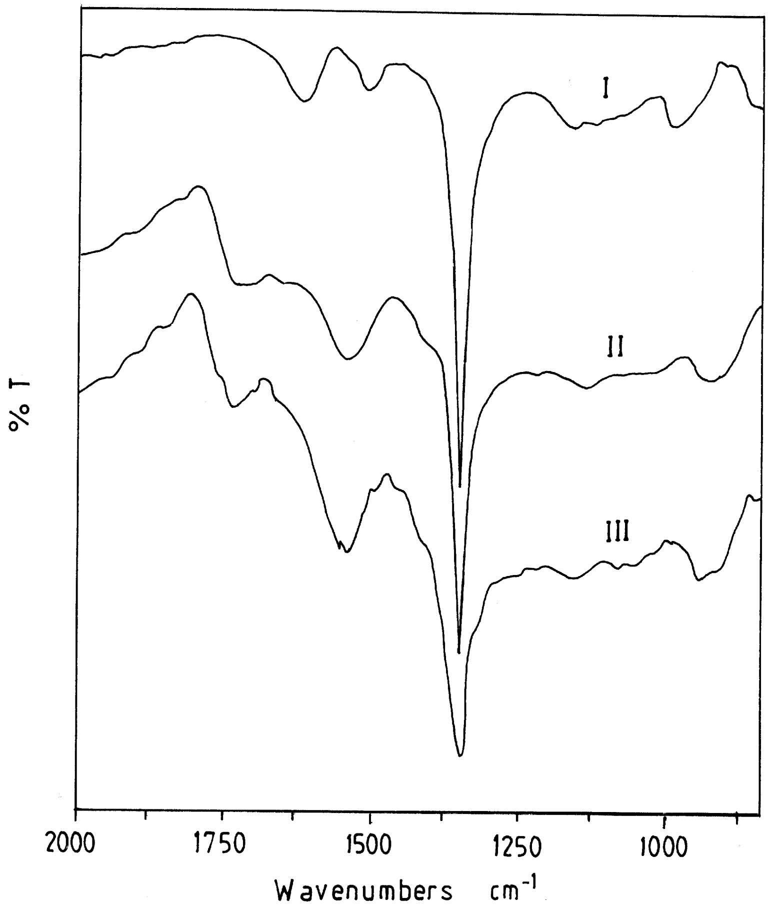

FIGURE 2 FTIR spectra of Py/*N*-methyl pyrrole copolymers prepared chemically by different Ce(IV) concentrations: I—0.05 M, II—0.1 M, III—0.15 M.

Because the free pyrrole, *N*-methyl pyrrole, and Ce(IV) do not have any absorbance at 450 nm alone (Figure 5, a and b), peaks 1–7 may be attributed to the soluble polymerization products of the reaction. In Figure 5, the increase in the Py concentration causes an increase in the absorbance at 450 nm, resulting in oligomeric products of copolymer, and reaches a constant value for all Py concentrations after 0.175 M.

The copolymerization yield also increases by increasing the Py concentration up to 0.175 M; at higher Py concentrations the yield is not affected. Similar investigation on *N*-methyl pyrrole concentration is given in Figure 6.

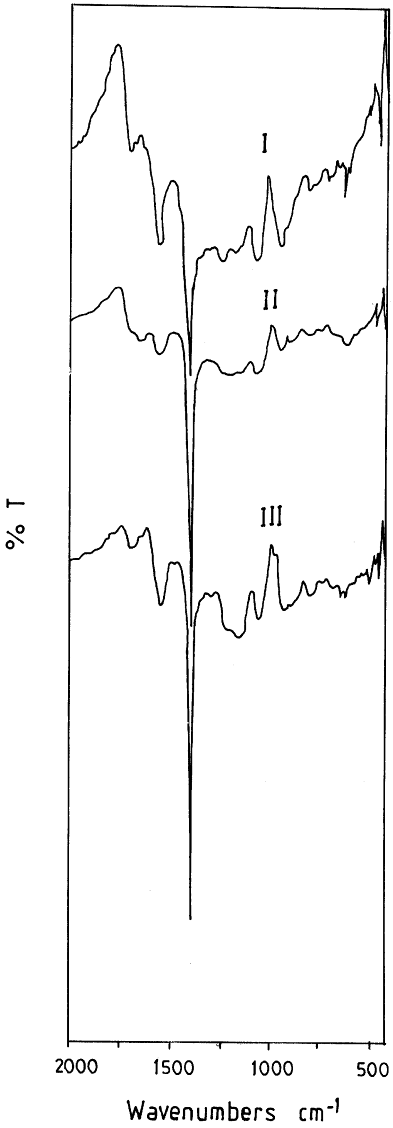

FIGURE 3 FTIR spectra of Py/*N*-methyl pyrrole copolymers prepared chemically by different Py concentrations: I—0.035 M, II—0.07 M, III—0.1 M.

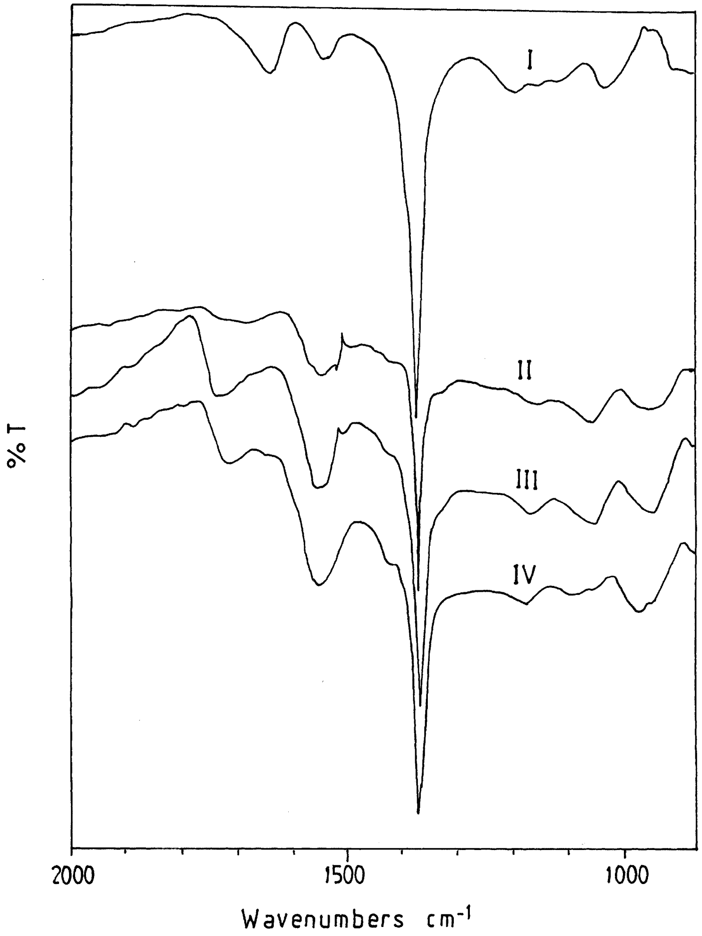

FIGURE 4 FTIR spectra of Py/*N*-methyl pyrrole copolymers prepared chemically by different *N*-methyl pyrrole concentrations: I—0.035 M, II—0.052 M, III—0.07 M, IV—0.1 M.

In contrast to the Py case, an increase in *N*-methyl pyrrole concentration caused a decrease in both yields and the absorbances of the soluble intermediates of copolymerization up to 0.175 M (Figure 7). This concentration seems to be critical for both pyrrole and *N*-methyl pyrrole inclusion into the copolymer structure at constant Ce(IV) salt concentration.

Figure 8 shows the relation of yield and absorbance values of soluble copolymerization products. Increase in Ce(IV) concentration increases

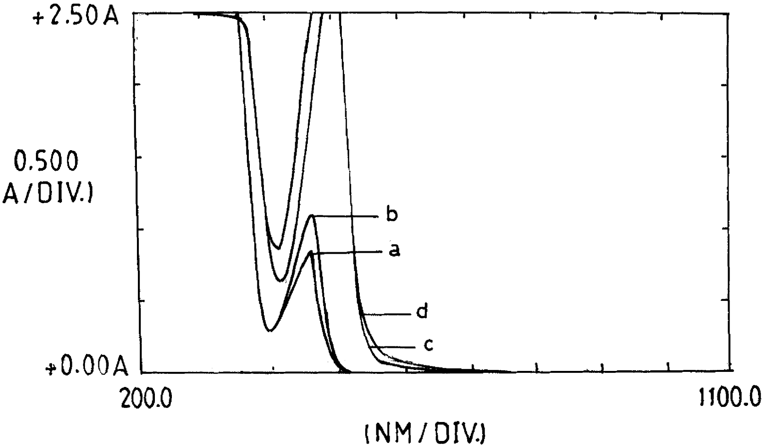

FIGURE 5 Absorbance spectra of reaction mixtures at different Py concentrations: (a) 0.035 M, (b) 0.1 M, (c) 0.175 M, (d) 0.35 M.

the copolymerization yield, while the absorbance values decrease up to 0.15 M Ce(IV) concentration. Further increase in Ce(IV) salt concentration does not affect the absorbances (Figure 8). But absorbance

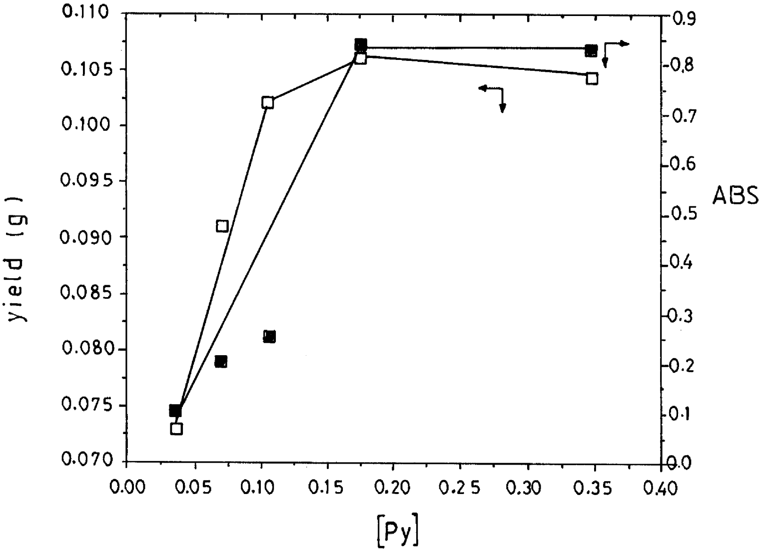

FIGURE 6 The effect of pyrrole concentration on the yield and absorbance values of soluble oligomers in the reaction medium.

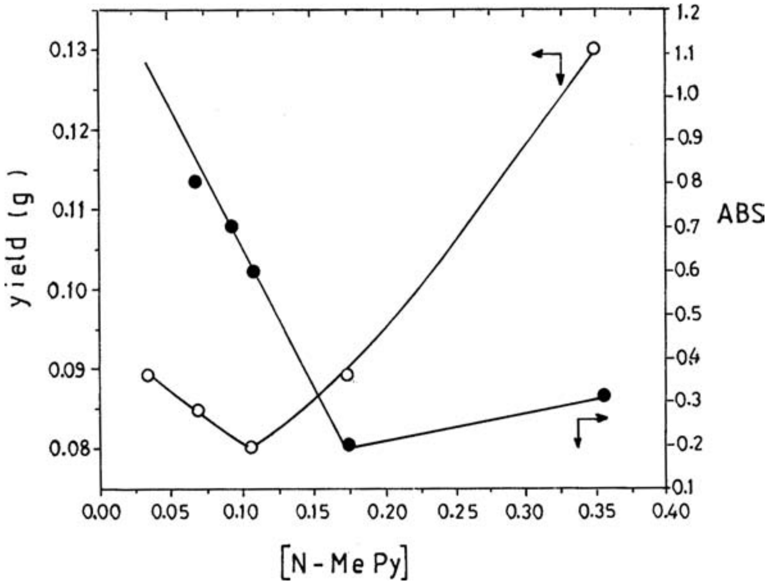

FIGURE 7 The effect of *N*-methyl pyrrole concentration on the yield and absorbance values of soluble oligomers in the reaction medium.

values increase, showing the formation of oligomeric soluble species formed in the presence of higher Ce(IV) and whose oxidation potential increases by increase in Ce(IV) according to the Nernst equation.

Kinetic Results

Determination of the reaction order relative to monomers, oxidant, and acid concentations was obtained from gravimetric results. The evolution of polymerization product weight with polymerization time for different Py concentrations was employed at constant Ce(IV), *N*-methyl pyrrole, and H_2SO_4 concentrations (0.10 M, 0.175 M, and 0.35 M, respectively). Rp values were obtained from the slopes of the weight-time lines for different pyrrole concentrations (Figure 9). Linear variations of the polymer weight against polarization time were observed. The physical meaning of the slopes is the rate of polymerization. Figure 10 shows an increase in Rp at increasing monomer concentrations. An order dependence on the monomer can be obtained from the slope of the Rp-concentration line. In the case of our experimental conditions the reaction orders were found as follows:

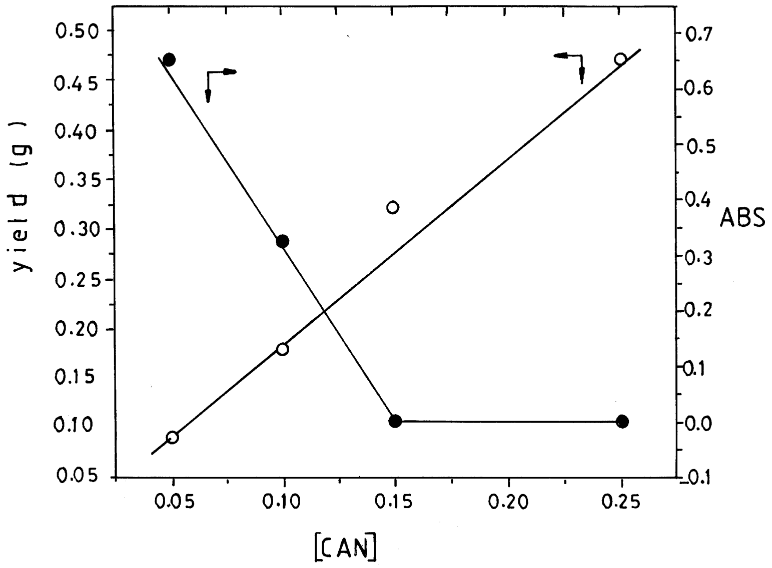

FIGURE 8 The effect of CAN concentration on the yield and absorbance values of soluble oligomers in the reaction medium.

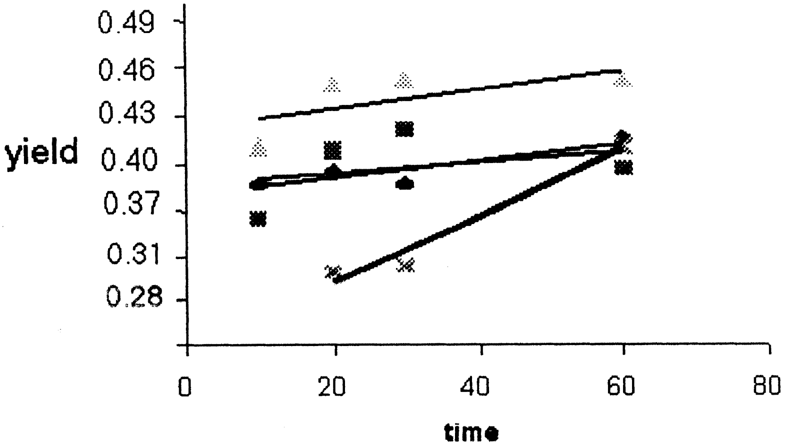

FIGURE 9 Evolution of copolymer weight with polymerization time for different Py concentrations: (a) 0.10 M, (b) 0.175 M, (c) 0.35 M.

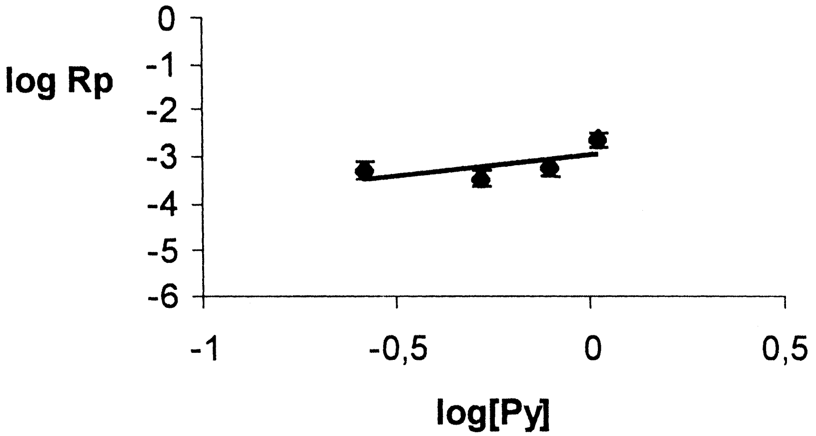

FIGURE 10 Determination of the reaction order relative to pyrrole concentration from gravimetric results (Rp values were obtained from the slopes of the weight-time lines for different Py concentrations).

$$\mathrm{Rp} = \mathrm{k[Py]}^{0.87}[\mathrm{N-Methylpy}]^{0.06}[\mathrm{Ce(IV)}]^{0.11}[\mathrm{H_2SO_4}]^{1.28}$$

Since it is known that pyrrole is more active than *N*-methyl pyrrole, the higher reaction order according to pyrrole than that for *N*-methyl pyrrole is an expected kinetic result.

Mechanism

It is not possible to describe a complete mechanism for the formation of the pyrrole–*N*-methyl pyrrole copolymer, since the important intermediates were not observed. However, the results can be used to extend previously reported mechanisms describing the chemical polymerization of pyrrole in solution[19].

The initial step is thought to be the formation of unstable pyrrole and *N*-methyl pyrrole radical cations, which can dimerize with the expulsion of H^+.

$$\mathrm{Py + Ce(IV) \dashrightarrow Py^{\cdot +} + Ce(III)}$$

$$\mathrm{NMPy + Ce(IV) \dashrightarrow NMPy^{\cdot +} + Ce(III)}$$

$$\mathrm{Py^{\cdot +} + NMPy^{\cdot +} \dashrightarrow Py - NMPy + 2H^+}$$

The polymer chain continues to grow as long as monomers and Ce(IV) are available:

$$\mathrm{Py - NMPy + Ce(IV) \dashrightarrow Py - NMPy^{\cdot +} + Ce(III)}$$
$$\mathrm{Py - NMPy^{\cdot +} + Py^{\cdot +}/NMPy^{\cdot +} \dashrightarrow}$$
$$\mathrm{Py - NMPy - Py/Py - NMPy - NMPy + 2H^{+}.}$$

Conductivity Measurements

Electrical conductivities were measured by using the four-probe technique, and it was found that the conductivity of the copolymers depends on Py concentration. As we change the Py concentration from 0.26 to 1.05 M, the conductivities of products change from 10^{-4} to 10^{-2} S/cm. Increase in *N*-methyl pyrrole does not increase the conductivities, probably due to overoxidation of the product, resulting in a pyrrolidone structure that is known as a structural defect in conjugation. CAN and H_2SO_4 concentration changes make very small differences in the conductivities.

CONCLUSION

Some important conclusions have been reached by discussing FTIR and UV-visible spectra and conductivity results. First, a higher pyrrole/*N*-methyl pyrrole ratio gave higher yield, absorbance values of soluble oligomers, and conductivity values of the resulting copolymer. FTIR spectra of products support the conclusion about the inclusion of *N*-methyl pyrrole into the PPy structure after the mole ratio of *N*-methyl pyrrole/CAN = 1.This inclusion is followed by a carbonyl peak due to the overoxidation in the case of *N*-methyl pyrrole present in the copolymer. Up to the ratio of $n_{N\text{-methyl pyrrole}}/n_{CAN} = 3.5$ the copolymerization yield and absorbance values decrease by increasing the *N*-methyl pyrrole concentration, then increase. Above the same ratio of $n_{Py}/n_{CAN} = 3.5$, there is no effect on either the yield or the absorbance values.

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