Chemical Polymerization of Pyrrole in the Presence of Ketone–Formaldehyde Resins

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ABSTRACT: The chemical polymerizations of pyrrole in the presence of acetophenone and formaldehyde, cyclohexanone, acetaldehyde, and formaldehyde, cyclohexanone and formaldehyde, cyclohexanone, resorcinol, and formaldehyde, cyclohexanone and lignosulfonate formaldehyde, and cyclohexanone, pyrrole, and formaldehyde were accomplished with Ce(IV) salt in acetonitrile solutions. The roles of the resin type, the addition order of the reactants, and the concentrations of the pyrrole and resin on the solubility and conductivity of the resulting products were investigated. The cyclohexanone–acetaldehyde–formaldehyde resin/polypyrrole copolymer had the highest solubility in dimethylformamide. The conductivity and solubility of the copolymers could be controlled by the Ce(IV)/pyrrole/resin molar ratio. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 618–624, 2005

Key words: conducting polymers; copolymerization; polypyrroles; redox polymers; resins

INTRODUCTION

Polypyrrole (PPy) exhibits good electrical conductivity and high air stability and is a potentially useful conductive polymer. It is produced as an insoluble powder, and this limits its applications in certain areas. To overcome the solubility problems of PPy, the oxidative polymerization of pyrrole (Py) in the presence of polyanions has been carried out,[1–6] and PPy, obtained as a ternary complex, stayed in a colloidal form. Another way of producing soluble PPy is to use special dopants. For example, PPy becomes solvent-soluble with a long-chain dopant such as dodecyl benzene sulfonic acid.[7] We recently described a polymerization method for producing PPy/ketonic resin copolymers.[8] The oxidative polymerization of Py by Ce(IV) was carried out in the presence of methyl ethyl ketone and formaldehyde resin. Although the insoluble PPy showed no glass-transition temperature (T_g), the produced conductive PPy copolymers were soluble in organic solvents and had T_g's. By the inclusion of ketonic resin segments, PPy possessed T_g and solubility.[8] The same method was used to prepare soluble and conductive silicone tegomer/PPy copolymers.[9] In this study, the effects of different types of ketonic resins on the conductivity, solubility, and thermal behavior of PPy/resin copolymers were investigated.

EXPERIMENTAL

Materials

Py, acetonitrile, dimethylformamide, acetone, and ceric ammonium nitrate (CAN) were all reagent-grade chemicals of the highest purity (Merck, Darmstadt, Germany) and were used without further purification.

Acetophenone–formaldehyde resin (AF-R), cyclohexanone–acetaldehyde–formaldehyde resin (CAsF-R), cyclohexanone–formaldehyde resin (CF-R), cyclohexanone–resorcinol–formaldehyde resin (CRF-R), cyclohexanone–lignosulfonate–formaldehyde resin (CLGSF-R), and cyclohexanone–pyrrole–formaldehyde resin (CPyF-R) were prepared according to procedures described elsewhere.[10–12] Ketonic resins and *in situ* modified ketonic resins were prepared in a three-necked flask. Ketone (1 mol), 0.1 mol of a modifier compound (e.g., acetaldehyde, resorcinol, Py, and lignosulfonate), and 1.6 mol of formaldehyde were added and heated to 60°C with stirring. Then, 2 mL of 20% NaOH was added in equal portions. When the temperature of the mixture rose to 80–90°C, refluxing began. After 3 h, the reaction was completed for CF-R and the modified resin. However, the reaction time for AF-R was about 16 h. The resin was purified through the decantation of the upper phase and several washes with hot water. It was then dried at 100°C *in vacuo*.

Analyses

Infrared spectra were recorded on a Jasco (Japan) FTIR 5300 Fourier transform infrared (FTIR) spectrometer.

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TABLE I
Effects of the Resin Type and Concentration on the Yield, Conductivity, T_m, and Solubility of the Copolymers

| Type of resin	Concentration of the resin ($[M] \times 10^3$)	Yield (g)	Conductivity $[(S/cm) \times 10^5]$	T_m of the copolymer (°C)	Solubility in acetone (mg/mL)
PPy[a] homopolymer	—	0.13	200	—	i
AF-R	2.1	0.12	3.7	78	10
	4.3	0.09	2.8	76	40
	8.6	0.14	2.0	—	70
	17	0.10	0.8	67	90
CAsF-R	2.1	0.08	20	76	10
	4.3	0.10	5.0	77	50
	8.6	0.16	0.4	82	110
	8.6[b]	0.09	8.0	—	i
	17	0.24	1.0	—	150
CF-R	2.1	0.13	130	90	0.8
	4.3	0.33	10	91	1
	8.6	0.46	0.7	95	1.3
	17	0.54	0.2	—	1.5
CRF-R	8.6	0.38	0.1	—	s
	13	—	0.5	—	s
CPyF-R	13	0.34	1.0	—	s
CLGSF-R[b]	8	0.5	0.6	81	s

[CAN] = 0.04; [Py] = 0.116. i = insoluble; s = soluble.
[a] PPy produced under the same conditions.
[b] The addition order of the components was CAsF, Py, and CAN.
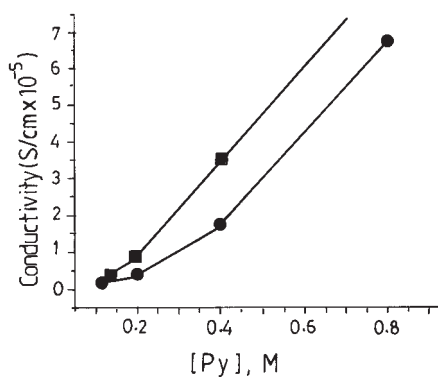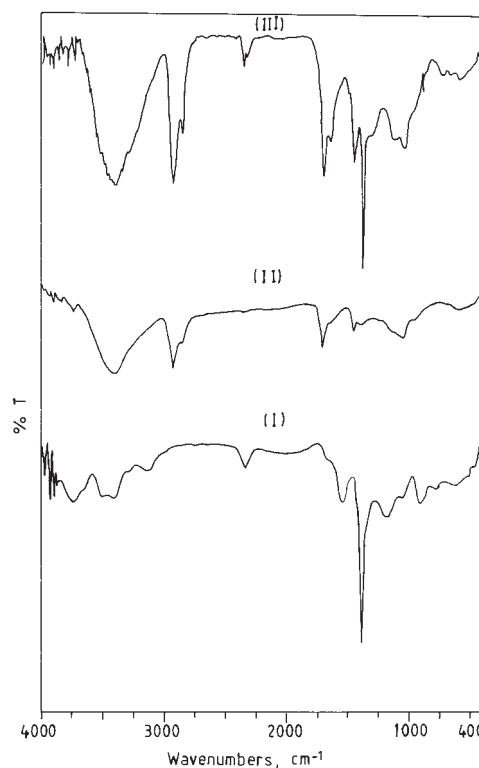

Figure 1 Effect of the Py concentration on the conductivity of (●) AF-R/PPy and (■) CAsF-R/PPy copolymers.
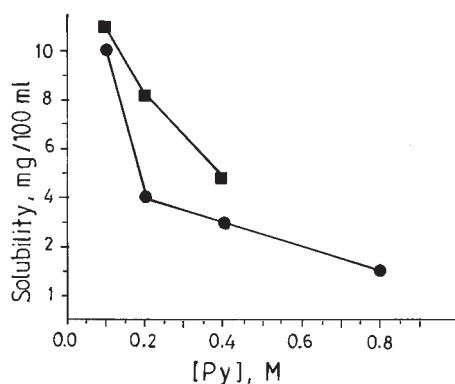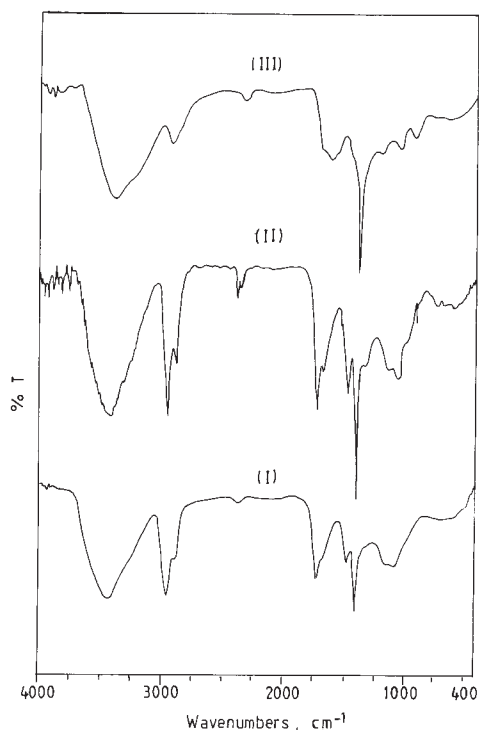

Figure 2 Effect of the Py concentration on the solubility of (●) AF-R/PPy and (■) CAsF-R/PPy copolymers.

The solubility properties of the block copolymers were investigated as follows. Some solid polymer in 2 mL of a solvent was mixed in a test tube at room

Figure 3 FTIR spectra of (I) the PPy homopolymer, (II) CAsF-R, and (III) the CAsF-R/PPy copolymer.

Figure 4 Effect of the CAN concentration on the spectra of the CAsF-R/PPy copolymer: (I) [CAN] = 0.01*M*, (II) [CAN] = 0.04*M*, and (III) [CAN] = 0.08*M*.

temperature and shaken. If the dissolution occurred in 5 min, it was considered soluble. A weighed solid copolymer sample was dissolved in 2 mL of a solvent in a test tube and then was filtered and weighed. The total dissolved copolymer was calculated from the weight difference. The insoluble parts of the copolymers were treated with excess solvent to determine the concentration of the PPy homopolymer.

Differential scanning calorimetry (DSC) thermograms were obtained with a PerkinElmer (United States) DSC-6 instrument; the heating rate was 10°C/min under a nitrogen atmosphere.

^{1}H-NMR spectra were obtained from dimethyl sulfoxide solutions and CDCl$_3$ on a Bruker (Germany) AC 250-MHz spectrometer. Chemical shifts [δ (ppm)] were reported downfield from tetramethylsilane.

Conductivity measurements

The copolymers were compacted under 10 tons of pressure to obtain thin pellets. The typical sample diameter was 13 mm, and the thickness was 0.8 mm. The conductivity measurements were performed with the four-probe technique and calculated with the following equation:

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

where σ is the conductivity, V is the potential (V), I is the current (A), and dn is the thickness (cm).

Chemical preparation of the ketonic resin/PPy copolymer

First, the ketonic resin, CAN, and Py were dissolved in acetonitrile separately. Then, the CAN solution was added to the resin solution dropwise with stirring in 5 min. The Py solution was added to the mixture, and a black powder formed almost instantaneously. After 1 h of polymerization, the powder was filtered, washed with acetonitrile several times, and dried at room temperature. The polymerization experiments were carried out at 25°C during stirring with a magnetic stirrer. The reaction volume was 40 mL in all experiments.

RESULTS AND DISCUSSION

The following are representative structures of the resins used in the copolymerization experiments:
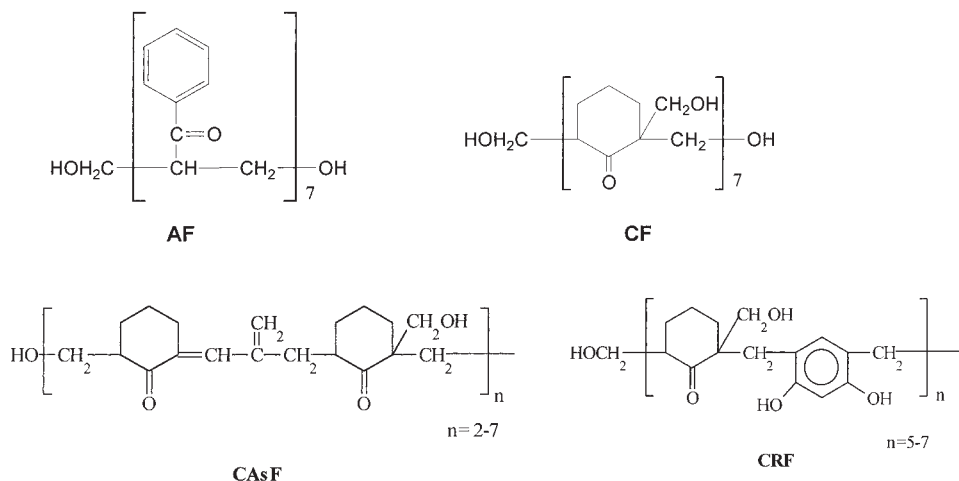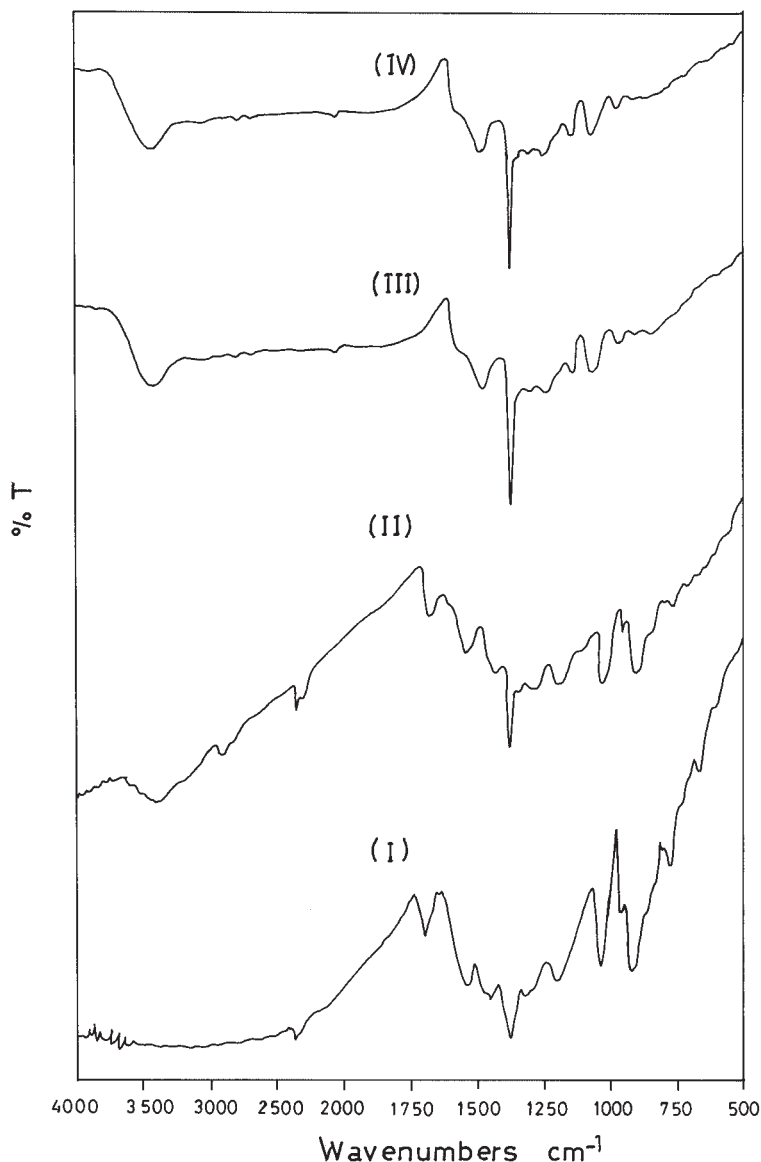
**Figure 5** FTIR spectra of (I) CF-R/PPy, (II) CLGSF-R/PPy, (III) AF-R/PPy, and (IV) CPyF-R/PPy copolymers.

The effects of the resin type and its concentration on the polymerization yield, conductivity, and solubility of the copolymers are listed in Table I. The copolymers did not contain any ketonic resin because they were washed with acetonitrile several times. Besides, the PPy homopolymers did not present in the copolymers produced with this system. The solubility values of the copolymers in Table I indicate that the given amount of the copolymer was completely soluble in the solvent.

The conductivity of the soluble copolymer (n_{CAN}/n_{Py} = 0.19) was like that of PPy obtained under the same conditions (ca. 10^{-3} S/cm).

The conductivity of the PPy/CF-R copolymer increased with increasing resin concentration, whereas this increase was not significant for the PPy/AF-R and PPy/CAsF-R copolymers (Table I). Although the CF-R/PPy copolymer had the highest conductivity value, its solubility was much lower. For CAsF-R, we obtained the highest solubility. Generally, increasing the resin concentration resulted in a reduction of the conductivity and an increase in the solubility (Table I). To determine the effect of the addition order of the reactants during the polymerization, we carried out the next experiment in the addition order of CAsF-R/PPy/CAN instead of CAsF-R/CAN/Py. In this case, the conductivity of the product was almost 10 times higher. However, the polymerization yield was much lower, and the product was insoluble (Table I).

Increasing the Py concentration increased the conductivity for the CFAs-R/PPy and AF-R/PPy copolymers (Fig. 1). An increase in the Py concentration reduced the solubility for the CFAs-R and AF-R/PPy copolymers (Fig. 2).
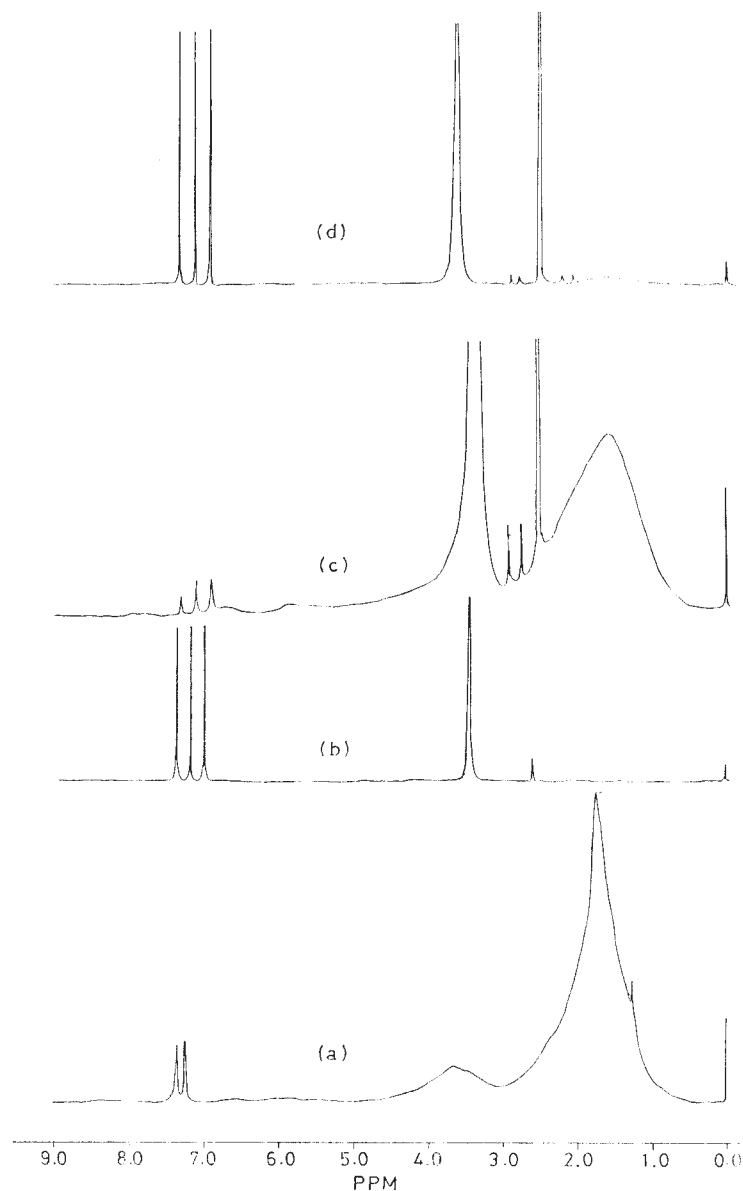
**Figure 6** ¹H-NMR spectra of (a) CF-R/PPy, (b) AF-R/PPy, (c) CAsF-R/PPy, and (d) CLGSF-R/PPy copolymers.

FTIR

The FTIR spectra of the chemically prepared PPy homopolymer, PPy prepared in the presence of CAsF-R, and CAsF-R alone are shown in Figure 3. Peaks due to carbonyl groups can be clearly seen, as well as peaks due to CAsF-R. The copolymer showed peaks at 3400 cm^{-1} due to methylol groups, at 1700 cm^{-1} due to carbonyl groups, at 2950 cm^{-1} due to aliphatic C—H vibration peaks, and at 1384 cm^{-1} due to NO_3^- ligands incorporated into the polymer. FTIR spectra of the CAsF-R/PPy copolymer according to the CAN concentration used are shown in Figure 4. Although the peak ratio of nitrate to carbonyl was the same, for the highest CAN concentration (line III, Fig. 4), this ratio was remarkably increased. The FTIR spectra of the CF-R/PPy, CLGSF-R/PPy, AF-R/PPy, and CPyF-R/

PPy copolymers are shown in Figure 5. Peaks due to the modifier compounds CF-R and AF-R can be clearly seen, as well as peaks due to the PPy segments and NO_3^- ligand. Resorcinol-, lignosulfonate-, and Py-modified CF-R and AF-R showed peaks at 800 cm^{-1} due to aromatic rings. The peak at 1384 cm^{-1} was due to NO_3^- ligands incorporated into the polymer. This peak always appeared as a sharp band in the spectra of the ketonic resin/PPy copolymers.

NMR

¹H-NMR spectra of the copolymers showed peaks at 6.9–7.3 ppm due to aromatic ring protons and at 0.8–4 ppm due to aliphatic protons. The signals of the methylene protons of the methylol groups appeared between 3 and 4.5 ppm. The ¹H-NMR spectrum of the

Initiation:

Propagation:

Termination:
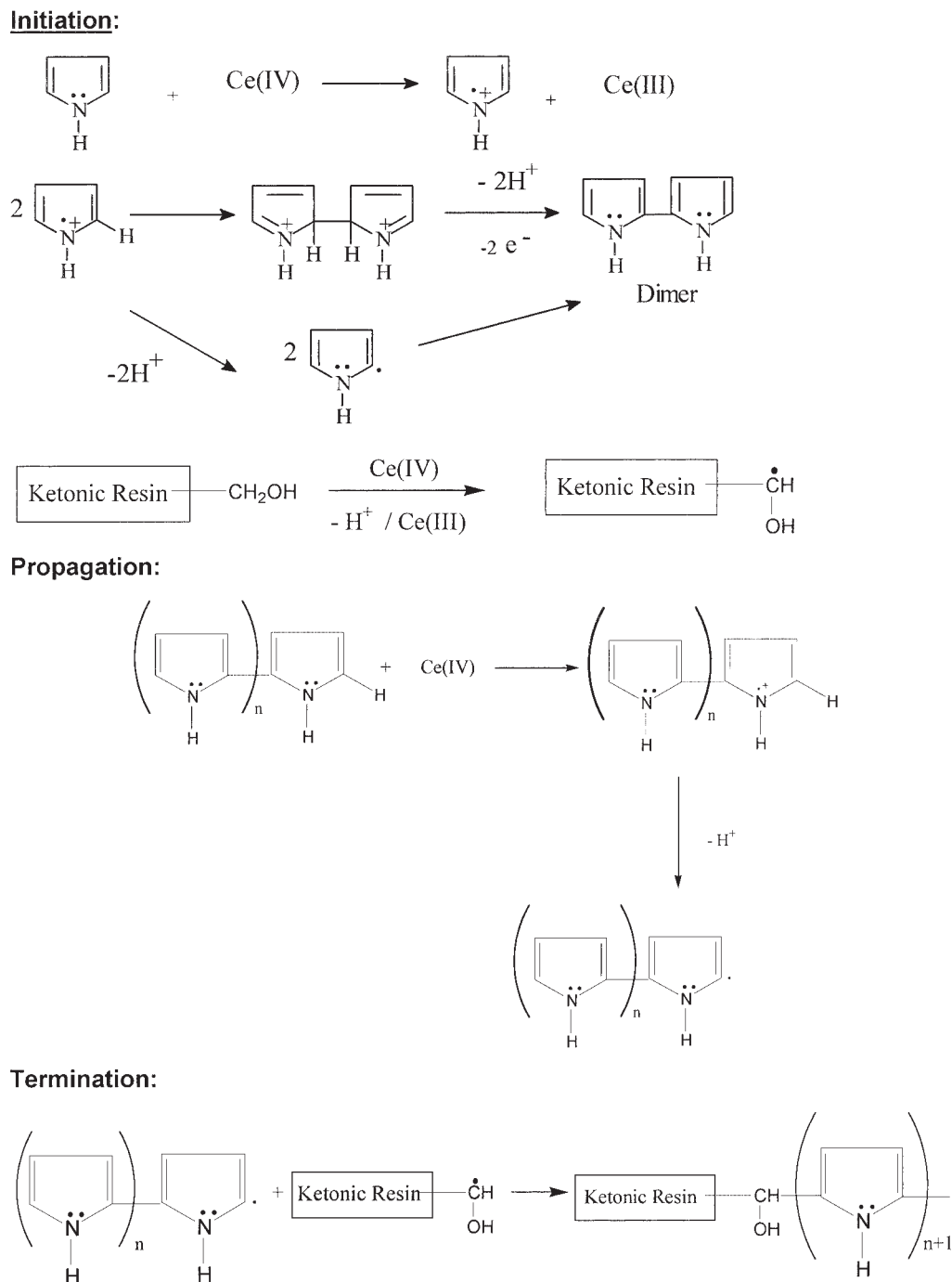
Scheme 1

CAsF-R/PPy copolymer showed a doublet at 6.8 and 7.0 ppm due to protons in the 3- and 4-positions of the Py ring [Fig. 6(c)].

Thermal analysis

CF-R, AF-R, and CAsF-R had melting temperatures (T_m's) of 110, 65, and 90°C, respectively.

The DSC scan of PPy showed no transition temperature (T_g or T_m), and this was a characteristic property of the PPy homopolymer. The CF-R/PPy, AF-R/PPy,

CAsF-R/PPy, and CLGSF-R/PPy copolymers had T_m values; the resin concentration did not seem to change them significantly. This was expected because the structure of the ketonic resin segment was not affected during the preparation of the copolymers.

Mechanism

The initial step in the chemical polymerization of Py is thought to be the formation of Py radical cations (Scheme 1). The oxidation of Py by Ce(IV)

forms radical cations (Py$^+$), which can dimerize with the expulsion of 2H$^+$ in the proposed mechanism for chemical synthesis, as suggested earlier.[8] The second mechanistic possibility in the initiation step is the proton loss of radical cations to form Py radicals, which dimerize. Ce(IV)/methylol redox reaction also occurs, and free radicals are generated in the initiation step.[13] In the propagation step, the polymer chains continue to grow as long as Py and Ce(IV) are available. In the termination step, the growing PPy chains may combine with ketonic resin radicals to produce PPy/ketonic resin copolymers.

CONCLUSIONS

AF-R/PPy, CAsF-R/PPy, CF-R/PPy, CRF-R/PPy, CLGSF-R/PPy, CPyF-R/PPy, and CPyF-R/PPy copolymers were prepared by the oxidative polymerization of Py with Ce(IV) in the presence of an appropriate ketonic resin. Most of the copolymers were soluble in common solvents. The conductivity values of these copolymers were varied through changes in the resin/Py/CAN ratio. Both soluble and fairly conductive ketonic resin/PPy copolymers were synthesized in acetonitrile. Moreover, the solubility and conductivity of the copolymers depended on the type of the ketonic

resin and the modifier of the *in situ* modified ketonic resin. Ketonic resin/PPy copolymers may be used in surface-coating applications for which conductivity is also an important property. The copolymers may find a number of new applications in addition to existing PPy applications.

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