

# Thermal Stability, Morphological, Dielectric, and Conductivity Characteristics of Pyrrole Modified Poly-*N*-Vinyl Carbazole

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## SYNOPSIS

*N*-vinyl-Carbazole (NVC) has been polymerized in the presence of pyrrole (PY) by anhydrous ferric chloride. The copolymer has been characterized by IR Spectroscopy. Thermal stability of P(PY-NVC) is intermediate between that of PNVC and PPY, respectively. DSC reveals a single glass transition break at 180–200°C for P(PY-NVC), which is higher than the  $T_g$  for polypyrrole ( $\sim 165^\circ\text{C}$ ), but is lower than that for PNVC ( $\sim 227^\circ\text{C}$ ). The XRD analysis reveals PPY to be totally amorphous and shows the percent crystallinity for P(PY-NVC) to be less than that of PNVC. Dielectric constants of the polymers follow the trend: PPY > P(PY-NVC) > PNVC, and fall sharply with the applied frequency to a limiting value. The polymers are characterized by a broad dielectric relaxation. DC conductivity is dependent on temperature and  $\text{FeCl}_3$ /polymer mole ratio and at a particular temperature follows the trend: PPY > P(PY-NVC) > PNVC. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(*N*-vinyl carbazole), PNVC, is well-known for its high thermal stability and interesting photo-physical and related characteristics.<sup>1–4</sup> Considerable research has been done to improve upon some of these properties by chemical modification of this polymer. In this context, it has been observed that pyrrole (PY), introduced as a comonomer during the solution polymerization of NVC by  $\text{FeCl}_3$ , yields a modified polymer, P(PY-NVC), which exhibits improved thermal stability and dielectric and conductivity characteristics, relative to those of unmodified PNVC. Geissler et al.<sup>5</sup> have reported their results on conductive polymer composites and copolymers of PY and NVC. As to the latter reaction, these authors have not referred to any details of purification and characterization of the reaction product. The general intractability of these polymers, PPY and P(PY-NVC), renders the usual sol-

vent separation process useless in this instance. In the absence of any such purification procedure, no bulk property can be unambiguously ascribed as specifically belonging to the copolymer and not to a mixture of PPY and PNVC. In this regard, the results of the present investigation are significant, as they suggest that DSC may be useful in establishing the identity of the products.

## EXPERIMENTAL

### Materials

Pyrrole (Merck-Schuchardt) was purified by vacuum distillation and was stored in a dark cool place. *N*-vinyl carbazole (BASF) was recrystallized from *n*-hexane before use. Anhydrous ferric chloride (Fluka) was used as obtained. All other solvents were of analytical grade and were freshly distilled before use.

### Polymerization

In a 250 mL, two necked Pyrex flask, equipped with a stirrer and nitrogen inlet tube, 2 mL of pyrrole

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(0.029 moles), 0.6 g  $\text{FeCl}_3$ , and 0.029 moles of NVC were dissolved in 100 mL of diethyl ether. The reaction continued for 24 h at 28°C with stirring under nitrogen atmosphere. The insoluble black mass P(PY-NVC) was first washed with 10% HCl, water, and boiling methanol, and was finally extracted, free of PNVC homopolymers, by refluxing with toluene for 1 h. Finally, the polymers were dried *in vacuo* for 6–8 h at 100°C.

## CHARACTERIZATION

### Spectroscopy

IR spectra of the polymers were taken on a Perkin-Elmer 883 IR Spectrophotometer in KBr pellets.

### Thermal Analysis

Thermogravimetry and Differential Scanning Calorimetry were performed on a Stanton Redcroft STA 625 model instrument.

### Morphology

Scanning electron micrographs were taken by CAM SCAN Series 2 DV.

### X-ray Scattering

The powdered samples were subjected to a wide angle X-ray diffraction study with the help of a PHILIPS PW/1710/00 X-ray diffractometer, using  $\text{CuK}_\alpha$  radiation.

### Dielectric Measurements

Dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) were recorded at different frequencies on a 4276-A HP LCZ Meter, Hewlett-Packard instrument with silver coated pellets of PPY, PNVC, and P(PY-NVC). The pellets were prepared under 5–6 tons of pressure.

### Electrical Conductivity

Electrical conductivity was obtained by using a cell containing guard ring and electrodes made of stainless steel discs. The DC conductivity was measured by a Keithley 617 solid state electrometer.

## RESULTS AND DISCUSSION

### General Features

P(PY-NVC) was recovered as a black powdery mass, insoluble in all solvents, including DMF and DMSO. Homopolymers of NVC and PY might eventually be formed in the polymerization system. PNVC was, however, removed by repeated extraction with boiling toluene. PPY was, as was P(PY-NVC), insoluble in all solvents and might possibly exist along with P(PY-NVC). Results of the DSC experiments confirmed, however, that under the experimental conditions that were followed, P(PY-NVC) was essentially obtained as a pure entity, free of PPY. A similar conclusion also followed from all other experimentation results, which indicated a distinct difference in pattern from those obtained with an arbitrary mixture of PNVC and PPY homopolymers.

### IR Absorption Characteristics

A comparative analysis of the IR spectra [Figs. 1(a) and (b)] of PPY, PNVC, and P(PY-NVC) was made to endorse the incorporation of PY in the PNVC chain. Table I summarizes the more important IR absorptions vis-a-vis their probable assignments. The incorporation of PY moiety in the PNVC chain is endorsed by these data.

### Morphological Characteristics

#### Scanning Electron Micrography

SEM of PPY, P(PY-NVC), and PNVC are presented in Figure 2. At 3  $\mu\text{m}$  magnification, PPY shows close packed agglomerates of irregular size and shapes. The presence of small spherical beads, distributed uniformly throughout the surface, is noted. PNVC SEM show particles of larger size. The agglomeration tendency is less and the presence of some spherical particles is detected along with irregular particles. In the case of the copolymer P(PY-NVC), the SEM is distinct from those of PPY and PNVC and shows distinctly formed spherical particles in evenly distributed agglomerates.

### X-ray Diffraction Characteristics

Figure 3 shows the XRD pattern for PPY, P(PY-NVC), and PNVC as a function of  $2\theta$ . As expected, PPY is totally amorphous with a strong halo in the angular region of 5–26° ( $2\theta$ ). The XRD pattern of PNVC reveals a partially crystalline structure, with

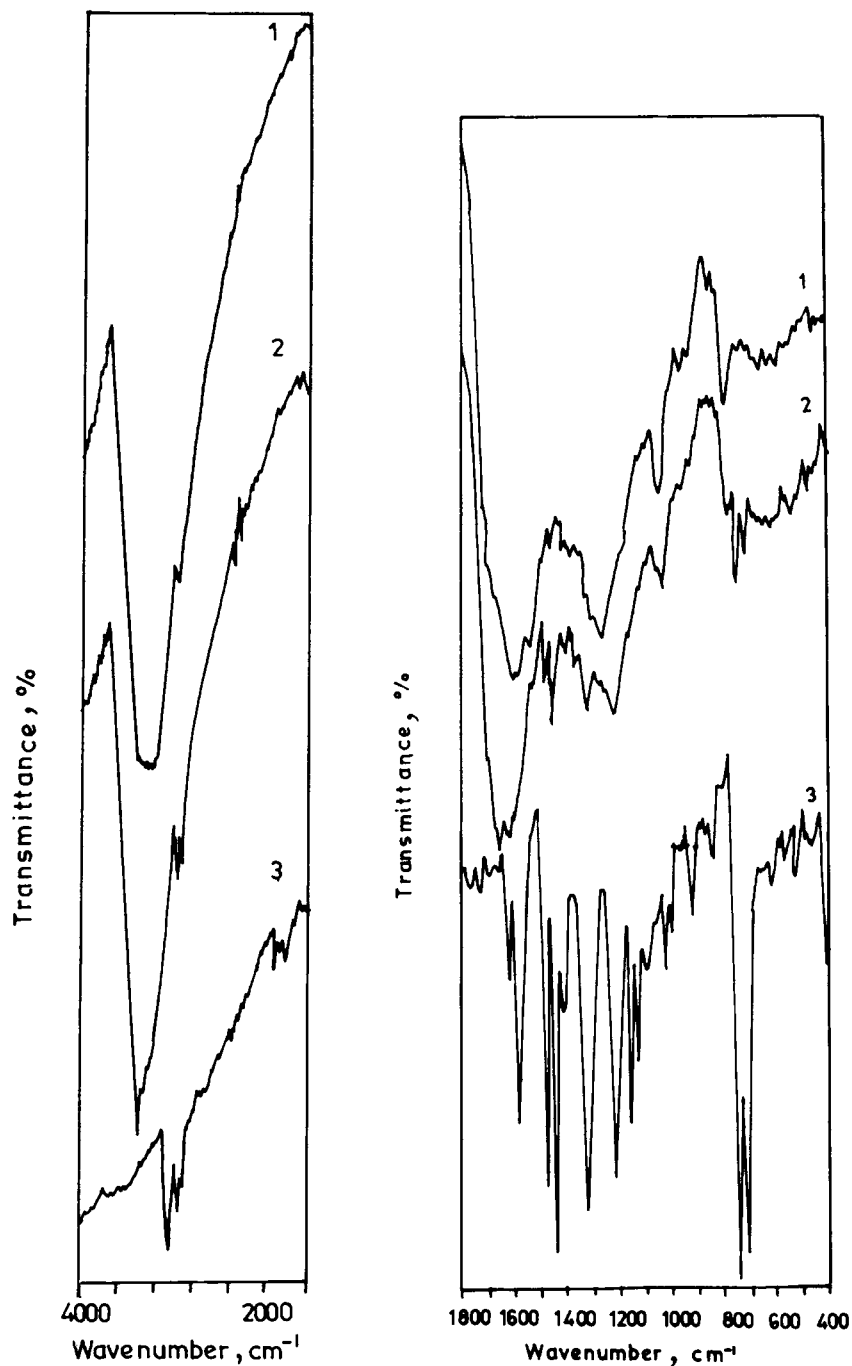


Figure 1 (a) and (b) IR spectra of (1) PPY (2) P(PY-NVC), and (3) PNVC.

peaks at  $13.4^\circ$ ,  $11.15^\circ$ ,  $9.7^\circ$ , and  $6.8^\circ$ . Several reports on the XRD of PNVC endorse the supposition that crystallinity depends on the nature of the initiating moiety and the polymerization condition, including temperature.<sup>14-16</sup>

The XRD pattern of P(PY-NVC) displays a pattern typical of either entity (PPY and PNVC):

a combination of broad amorphous structures and a partially crystalline pattern ( $2\theta$  at  $13.8^\circ$ ,  $12.4^\circ$ ,  $9.7^\circ$ , and  $8.9^\circ$ ). Clearly, two new peaks *viz.*  $12.4^\circ$ ,  $8.9^\circ$  appear in the XRD for P(PY-NVC), corresponding to a different interplaner distance.

After heating above the glass transition temperatures, the XRD patterns of both PNVC and P(PY-

**Table I Band Assignments of PPY, PNVC, and Copolymer**

Observed Peaks (cm <sup>-1</sup> )			
PPY	Copolymer	PNVC	Assignment of Peak
3309	3417	—	H-bonded N—H stretching <sup>9,a</sup>
—	2972	2968	C—H asymmetric stretching for aromatic C—H group
—	2932	2928	
2316	2326	—	Aromatic ring vibration of pyrrole
—	1659	1640	C=C stretching of vinylidene group <sup>10</sup>
—	1625	1622	
1530	1525	—	1,2 di- or trisubstituted pyrrole <sup>11</sup>
—	1481	1481	Ring vibration of NVC moiety
—	1451	1448	
—	1406	1405	> CH <sub>2</sub> deformation of vinylidene group
—	1327	1329	C—H in plane deformation of vinylidene group
—	1228	1220	C—H in plane deformation of aromatic ring
1047	1046	—	C <sub>β</sub> —H vibration of 1,2,5 or 1,3,4 substitution of pyrrole <sup>12</sup>
930	932	—	1,3,4 trisubstitution of pyrrole <sup>13</sup>
785	783	—	1,3,4 trisubstitution of pyrrole ring <sup>13</sup>
—	752	746	> CH <sub>2</sub> rocking vibration, due to tail-tail addition (CH <sub>2</sub> ) <sub>2</sub> group <sup>13</sup>
—	724	721	Ring deformation of substituted aromatic structure <sup>13</sup>

<sup>a</sup> Due to copolymerization, the degree of H-bonding is reduced, hence higher frequency is observed for copolymer.

NVC) do not indicate any major change in the features. However, a minor increase in the crystallinity is observed. The crystalline peaks are sharper in the heated sample. Table II compares the % crystallinity for PNVC and P(PY-NVC), subjected to ambient and elevated temperatures. The % crystallinity was estimated by the relation  $X_e = \frac{I_c}{I_c + I_a} \times 100$ , due to Hermans and Weidinger,<sup>17</sup> where,  $I_c$  and  $I_a$  are the integrals of the crystalline and amorphous peaks, respectively.

### Thermal Stability Characteristics

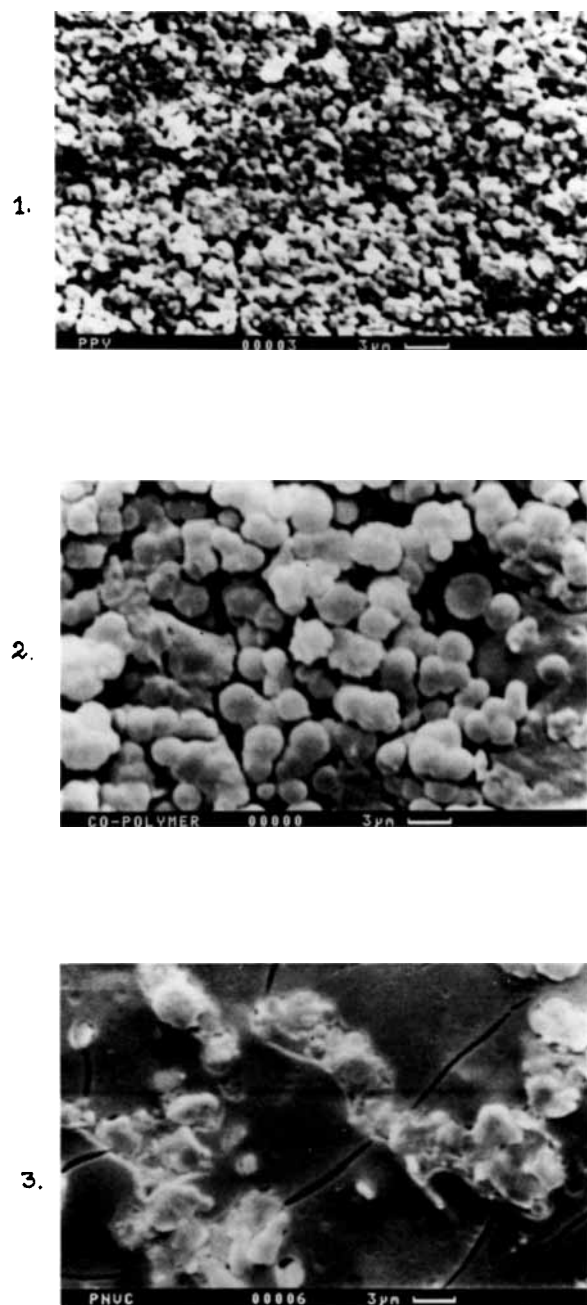
Table III presents the percent weight loss at different temperatures for PPY, PNVC, and P(PY-NVC). These data endorse the thermal stability of P(PY-NVC) to be intermediate between those of PNVC and PPY, respectively. In case of PNVC after the initial degradation, the weight loss occurs sharply up to 475°C, and then the rate of weight change becomes slower up to 600°C. For PPY and P(PY-NVC), however, the weight loss after the initial decomposition temperature continues sharply up to a temperature of 550°C. Weight residues, corresponding to the maximum temperature recorded, were ca. 10%. Further, 50% weight loss occurs at

400°C in the case of PPY, at 450°C for PNVC, and at 425°C for P(PY-NVC), respectively.

For homopolymers of PY and of NVC, a single break manifests at ~ 165°C and at ~ 227°C, respectively in the DSC scan. For P(PY-NVC), a single break appears in the range 180–200°C. Further, a mixture of (1 : 1 w/w) PPY and PNVC reveals two breaks at 163° and 228°C. The reported<sup>2</sup>  $T_g$  value for PNVC is 225° ± 2°C; however, the  $T_g$  is reportedly<sup>2</sup> sensitive to traces of impurities and molecular weight. In view of the observed agreement in the experimental  $T_g$  value of PNVC with the literature value, it appears probable that the break at ~ 165°C for PPY in the DSC of PPY will correspond to its  $T_g$ . Unfortunately, information in the literature corroborating this data have not been available, despite a thorough search.

The appearance of a single break in the DSC of P(PY-NVC) is expected if P(PY-NVC) is present as a single entity and not as a mixture of PPY homopolymer and P(PY-NVC). The latter contention is already endorsed by the DSC results for the mixture. Hence, these data appear to imply that under the present experimental conditions, P(PY-NVC) exists as a pure copolymer and not as a mixture of P(PY-NVC) and PPY.

The manifestation of a  $T_g$  for P(PY-NVC), lower than the same for PNVC, is, in addition, consistent



**Figure 2** Scanning electron micrographs of (1) PPY (2) P(PY-NVC), and (3) PNVC at 3  $\mu\text{m}$  magnification.

with the internal plasticization effect,<sup>18</sup> introduced by the copolymerized moieties in the P(PY-NVC) chain.

DSC thermograms reveal an exothermic peak at 300°C with two smaller peaks at 450°C and 520°C, respectively, for P(PY-NVC). The DSC scan for PPY is similar, but the peaks are less sharp. It is

obvious from the DSC scan that major structural degradation occurs in the range 300°–550°C and that it involves thermooxidative cleavage of the aromatic linkages in the polymer matrix.

### Dielectric Characteristics

Figures 4 and 5 represent the variation of dielectric constant ( $\epsilon$ ) and loss ( $\tan \delta$ ) parameters for PPY, P(PY-NVC), and PNVC, with the applied frequency. Both of these parameters exhibit a monotonic fall with the applied frequency to a limiting value. At low frequency ( $\sim 100$  Hz), PPY is characterized by a high dielectric constant (57.2), relative to either PNVC (6.0) and P(PY-NVC) (10.5). Further, the fall in these parameters is less sharp in PNVC or P(PY-NVC). With the frequency increasing in the range 100 Hz to 50 KHz, PPY shows *ca.* a 90%, PNVC shows a 28%, and P(PY-NVC) shows a 65% fall in the dielectric constant value.

In general, the  $\tan \delta$ -frequency trend is indicative of a broad relaxation in all these systems. The dielectric-frequency curves are otherwise featureless in all these cases, which rules out, as expected, any group loss.<sup>19</sup>

The general trend observed in these systems is reminiscent<sup>1,6-8</sup> of the situation encountered in other *N*-bearing polymerization systems. A high dielectric constant in PPY at a low frequency is consistent with a conjugated structure, which will facilitate the frequency-induced dielectric polarization. Apparently, the copolymerization of NVC with PY does not result in a highly conjugated structure, which accounts for a lower dielectric constant as compared to PPY at a comparable frequency.

### Conductivity

Figures 6 and 7 represent the conductivity vs. temperature plots for PPY, P(PY-NVC), and PNVC. These data reveal the following features in particular: (i) At a fixed  $\text{FeCl}_3$  concentration (0.0037

**Table II** Effect of Heating on % Crystallinity

Polymer	$X_c$ (% Crystallinity)	
	Ambient temperature	Heated $> T_g$
PNVC	21.9	24
P(PY-NVC)	3.1	4

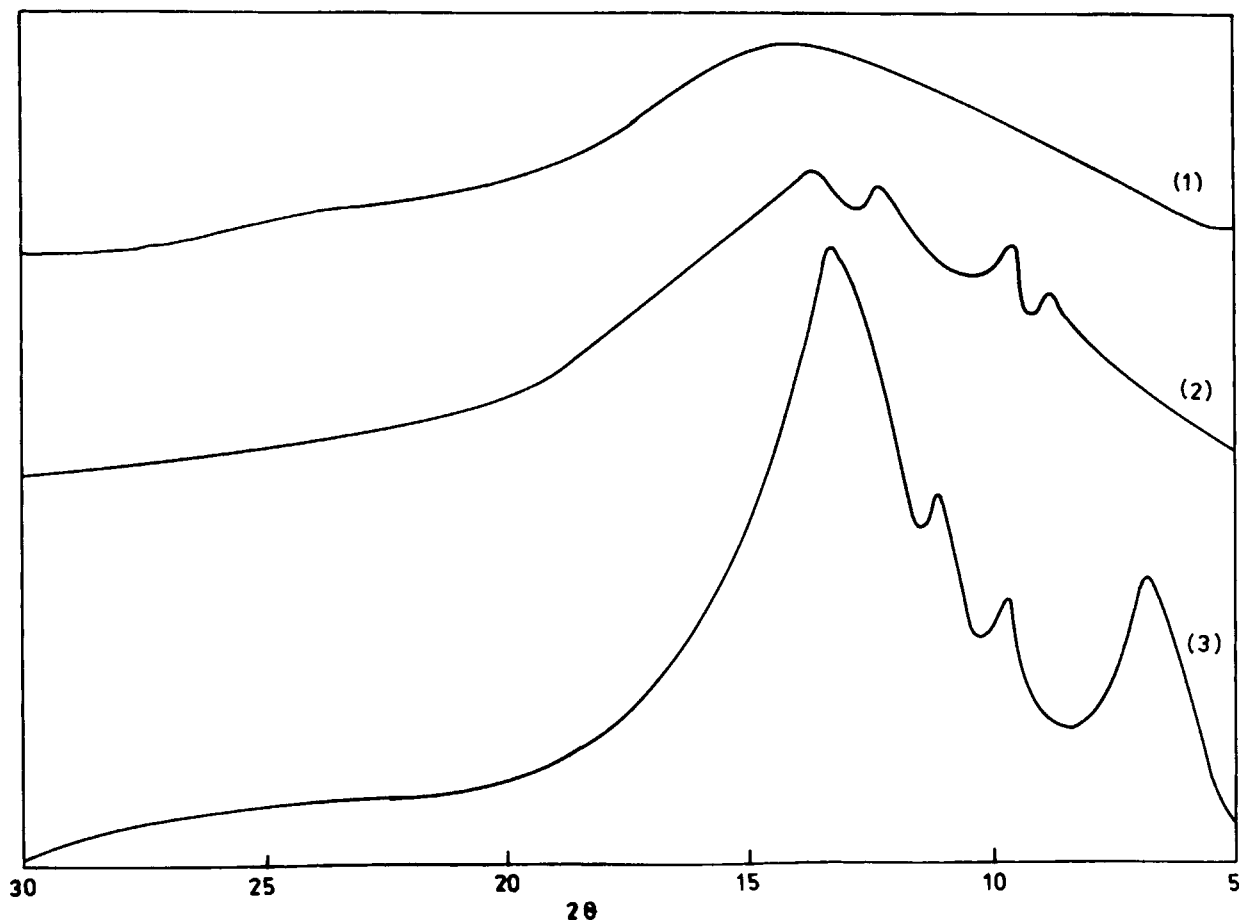


Figure 3 X-Ray diffractograms of (1) PPY, (2) P(PY-NVC), and (3) PNVC.

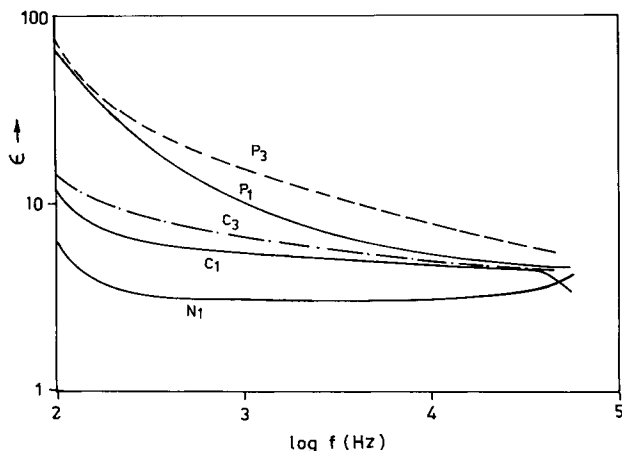
moles), PNVC shows specific conductivity in the order ( $S\text{ cm}^{-1}$ ) of  $10^{-10}$  (1.8 to 2.45), PPY (1.65 to  $4.67 \times 10^{-5}$ ) and P(PY-NVC) ( $3.7$  to  $7.24 \times 10^{-6}$ ) in the temperature range 298–422 K. Thus, PNVC exhibits only a marginal change in conductivity with

temperature. PPY shows a relatively higher positive temperature coefficient, while P(PY-NVC) reveals an intermediate behavior; (ii) The effect of the  $\text{FeCl}_3$  concentration on the conductivity is shown in Figure 7, which suggests that the conductivity of PNVC is

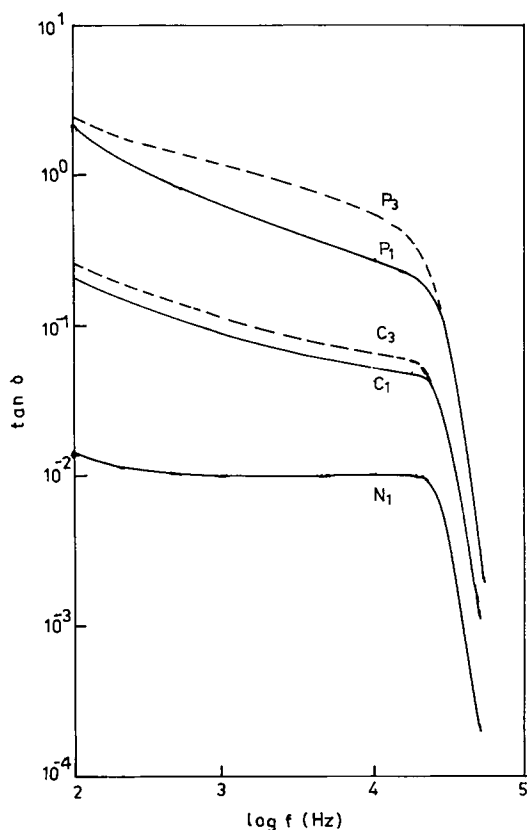
Table III Thermal Stabilities of PPY, PNVC, and P(PY-NVC)

Polymer	Moles			Temperature ( $^{\circ}\text{C}$ ) for Decomposition of Polymer (%)				Glass Transition Temperature ( $^{\circ}\text{C}$ )
	(NVC)	(PY)	( $\text{FeCl}_3$ )	Initial ( $T_i$ )	20	50	70	
PPY	—	0.029	0.0037	210	255	400	486	165
PNVC	0.029	—	0.0037	350	399	450	467	227
P(PY-NVC)	0.029	0.029	0.0037	252	317	425	497	200 <sup>a</sup>
P(PY-NVC)	0.029	0.029	0.0074	260	327	428	486	190 <sup>a</sup>
P(PY-NVC)	0.029	0.029	0.0148	262	350	466	527	180 <sup>a</sup>

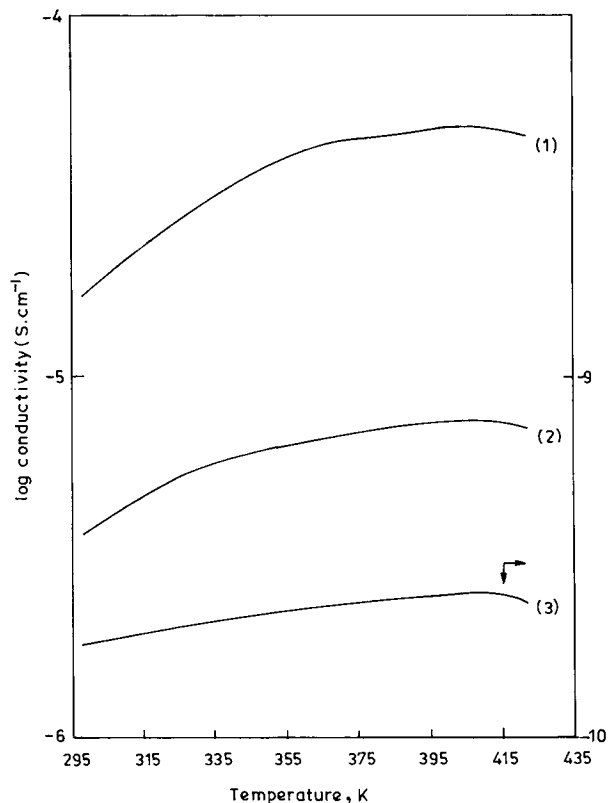
<sup>a</sup> A mixture (1 : 1) of PNVC and PPY revealed two glass transition breaks corresponding to  $228^{\circ}\text{C}$  and  $163^{\circ}\text{C}$ , respectively.



**Figure 4** Dielectric constant vs. frequency plots of  $P_1$  = PPY (0.0037),  $P_3$  = PPY (0.0148),  $C_1$  = P(PY-NVC) (0.0037),  $C_3$  = P(PY-NVC) (0.0148), and  $N_1$  = PNVC (0.0037). (Numbers in parentheses denote concentrations of ferric chloride.)



**Figure 5** Dielectric loss vs. frequency plots of  $P_1$  = PPY (0.0037),  $P_3$  = PPY (0.0148),  $C_1$  = P(PY-NVC) (0.0037),  $C_3$  = P(PY-NVC) (0.0148), and  $N_1$  = PNVC (0.0037). (Numbers in parentheses denote concentrations of ferric chloride.)

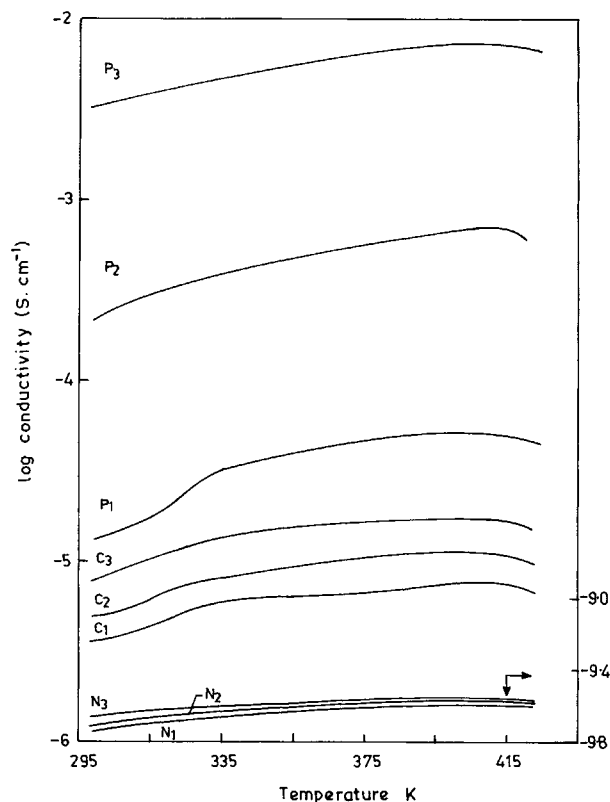


**Figure 6** Conductivity vs. temperature plots of (1) PPY (0.0037), (2) P(PY-NVC) (0.0037), and (3) PNVC (0.0037). (Numbers in parentheses denote concentrations of ferric chloride.)

marginally increased with the  $\text{FeCl}_3$  concentration, while for PPY, the effect is more conspicuous. Thus, with increasing amounts of  $\text{FeCl}_3$  from 0.0037 M to 0.0148 M, the conductivity increases by a factor of 100 (408 K). P(PY-NVC) shows a similar trend, but the temperature coefficient is less as compared to PPY. The effect of the  $\text{FeCl}_3$  concentration on the conductivity of the copolymer is less pronounced; thus at 298 K, a four-fold increase in the  $\text{FeCl}_3$  concentration results in a two-fold increase in conductivity.

Regarding these conductivity values, the range of conductivity values realized for PPY is consistent with the observation of Myers,<sup>20</sup> who suggested that the conductivity of PPY is characteristically dependent on the  $\text{FeCl}_3$ /Pyrrole mole ratio. Significantly, an extrapolation from the conductivity vs.  $\text{FeCl}_3$ /Pyrrole mole ratio curve, reported by Myers,<sup>20</sup> indicates that with the 0.125 mole ratio, as used in this case, the conductivity should be on the order of  $10^{-5} \text{ S cm}^{-1}$ , as was actually observed.

Attempts to use higher mole ratios of  $\text{FeCl}_3$ /Pyr-



**Figure 7** Conductivity vs. temperature plots of  $P_1$  = PPY (0.0037),  $P_2$  = PPY (0.0074),  $P_3$  = PPY (0.0148),  $C_1$  = P(PY-NVC) (0.0037),  $C_2$  = P(PY-NVC) (0.0074),  $C_3$  = P(PY-NVC) (0.0148),  $N_1$  = PNVC (0.0037),  $N_2$  = PNVC (0.0074), and  $N_3$  = PNVC (0.0148). (Numbers in parentheses denote concentrations of ferric chloride.)

role for achieving higher conductivity values were abandoned, since even the homopolymer PNVC became intractable under these conditions, thereby rendering the separation virtually impossible.

It has currently been observed<sup>21</sup> in this context that a change of solvent using water<sup>22</sup> as one of the components helps to improve the conductivity dramatically. Thus, under ambient temperature, it has been possible to prepare<sup>21</sup> PPY and PNVC by suspension polymerization in the presence of  $\text{FeCl}_3$ , with conductivity on the order of 4 and  $10^{-4}$   $\text{S cm}^{-1}$ , respectively. The copolymerization behavior under this condition is currently being explored in detail.

## CONCLUSION

Copolymers, synthesized from NVC and PY with anhydrous ferric chloride, show improvement in

thermal stability with respect to PPY, while dielectric and conductivity characteristics are considerably improved with respect to PNVC.

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