NOTE

Ferric Chloride-Initiated Polymerization of Pyrrole in Presence of *N*-Vinyl Carbazole in Aqueous Suspension

INTRODUCTION

In continuation of our ongoing research on the chemical modification of pyrrole (PY)-based polymers, we reported the polymerization of PY in the presence of *N*-vinylcarbazole (NVC) by $FeCl_3^I$ and by an organic electron-transfer agent, *O*-Chloranil (*O*-CA)[2], in nonaqueous solvents. In either system, the product is an insoluble black polymer, P(PY–NVC), which exhibits characteristics of both PY and NVC moieties in the IR spectra and bulk properties like thermal stability, dielectricity, and conductivity, which are distinct from either of the two homopolymers. Significantly, the dc conductivity of P(PY–NVC), thus prepared, falls in the range of $\sim 10^{-3} S\ cm^{-1}$.

We report now that by using an aqueous medium, in which a toluene solution of NVC and PY is kept in suspension, the conductivity of P(PY–NVC) can be enhanced almost 10^3-fold using $FeCl_3$ as the catalyst. Other bulk properties, however, such as thermal stability or the electrical characteristics of P(PY–NVC), are not significantly altered by changing the polymerization solvent.

EXPERIMENTAL

Materials

Pyrrole (PY) (Merck-Schuchardt) was purified by vacuum-distillation and was stored in a dark cool place. NVC (BASF) was recrystallized from *n*-hexane before use. Anhydrous $FeCl_3$ (Fluka) was used as obtained. Water was double-distilled. All other solvents were of analytical grade and were freshly distilled before use.

Polymerization

As NVC is insoluble in water, the suspension polymerization of this monomer was performed in a biphasic system. Calculated quantities of NVC and PY were dissolved in a known minimum volume of toluene and the solution was added to water containing the desired amount of $FeCl_3$. The mixture was continuously stirred under a nitrogen atmosphere. Almost instantaneously, the solution turned

black, indicating the onset of polymerization. The reaction was continued for 6 h. The resulting black powder was filtered and dried in air. Then, it was extracted with toluene to remove unreacted monomer and homopolymer (PNVC), finally washed with boiling methanol to remove any unreacted NVC and the $FeCl_3$ coloration, and dried at 80°C for 8 h under *vacuo*.

Characteristics

IR spectra were recorded on a Perkin-Elmer 883 IR spectrophotometer in KBr pellets. Thermogravimetry and differential scanning calorimetry were performed on a Stanton Redoroft STA 625 instrument. Scanning electron micrographs were taken by a CAMSCAN, Series 2 DV. Dielectric constants and the loss factors were recorded at different frequencies on a Hioki 3530 LCR Hitester instrument with silver-coated pellets prepared under 5–6 ton pressure. Dc conductivity measurements were performed on a Kiethley 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 also insoluble in all solvents and might possibly exist along with P(PY–NVC). However, P(PY–NVC) obtained earlier by us in $FeCl_3$ ether[1] or the *O*-CA toluene system[2] was found to behave as a pure compound and not as a mixture [single glass transition break, reproducible thermogram, and reproducible IR data, different from those of a mixture of PPY and P(PY–NVC)]. Similar features observed with the present system appeared to suggest that P(PY–NVC) also exists as a single compound and not contaminated with PPY.

Results of C, H, N analysis for P(PY–NVC) (Table I) indicated % C = 67.54, % H = 4.92, and % N = 8.15. These data correspond to a C/N ratio = 8.2, while the

Table I   Polymerization and Conductivity Characteristics of PPY, PNVC, and P(PY–NVC)

Polymer	Mol $\times$ 10^{-3}			Yield (%)	Conductivity S cm^{-1}
	NVC	PY	FeCl$_3$		
PPY	—	7.2	29	90	6.12 $\times$ 10^{-2}
PPY	—	7.2	58	89	9.48 $\times$ 10^{-2}
PNVC	7.2	—	29	36	4.25 $\times$ 10^{-5}
P(PY–NVC)	7.2	7.2	29	43	2.19 $\times$ 10^{-3}
P(PY–NVC)	7.2	7.2	58	45	2.17 $\times$ 10^{-3}
P(PY–NVC)[a]	7.2	7.2	116	45	3.5 $\times$ 10^{-3}
P(PY–NVC)[b]	29	29	3.7		3.7 $\times$ 10^{-6}
P(PY–NVC)[c]	2.6	7.25	2.03[d]	32	3.5 $\times$ 10^{-6}

[a] (%) C, H, N, Cl data reported in text.
[b] Diethyl ether was used as the solvent medium.
[c] Toluene was used as the solvent medium.
[d] o-Chloranil was the catalyst.

same for P(NVC) and PPY are, respectively, 12 and 3. It would be tempting to ascribe the observed C/N ratio for P(PY–NVC) to a 1 : 1 copolymer. However, P(PY–NVC) is likely to contain besides "Cl" (11%), other elements (Fe from the catalyst).[3,4] Hence, it would not be justified to draw any definite conclusion regarding the structure of P(PY–NVC) on the basis of these data alone.

IR Absorption Characteristics

The N—H stretching vibration (Table II) of PPY occurs at 3400 cm^{-1}. The corresponding N—H stretching of P(PY–NVC) appears at a higher frequency (3444 cm^{-1}), indicating a reduction in the degree of H-bonding due to copolymerization. The 2930 cm^{-1} peak of P(PY–NVC) corresponds to the C—H asymmetric stretching of the aromatic ring arising from NVC moiety, while the 2334 cm^{-1} peak corresponds to the heterocyclic ring vibration and the 1647 cm^{-1} and 1625 cm^{-1} doublet of PNVC is due to the C=C stretching vibration of vinylidene group which merges in 1638 cm^{-1}. A shoulder at 1600 cm^{-1} and two peaks at 1478 and 1446 cm^{-1} arise from the ring vibration of the NVC moiety. The 1044 cm^{-1} is the characteristic absorption peak for the C—H stretching vibration of the 1, 2, 5- or 1, 3, 5-trisubstituted pyrrole ring. The peak at 780 cm^{-1} is due to 1, 3, 4-trisubstituted pyrrole.

Table II   IR Band Assignments of PPY, PNVC, and P(PY–NVC)

| Observed Peaks (cm^{-1})			Assignments
PPY	P(PY–MVC)	PNVC	
3400	3444	—	N—H stretching band of PPY[5]
	2930	2931	Aromatic C—H asymmetric stretching
	2334	2336	Heterocyclic ring vibration
	1638	1647/1625	C=C stretching of vinylidene group[6]
	–1600 (Shoulder)	1597	Ring vibration of NVC moiety
1542	1544	—	C=C stretching vibration of trisubstituted pyrrole
	1478	1483	Ring vibration of NVC moiety
	1446	1450	
1040	1044		C—H stretching vibration of 1,2,5- or 1,3,4-trisubstituted pyrrole[7]
777	780	—	1,3,4-trisubstitution of pyrrole ring
	744	746	aromatic out of plane C—H bending[8]
	720	721	Ring deformation of substituted aromatic structure[8]

The peak at 780 cm^{-1} is due to 1, 3, 4-trisubstituted pyrrole. The 744 cm^{-1} peak of P(PY–NVC) may be attributed to the aromatic out of plane C—H bending due to incorporating a NVC moiety. In P(PY–NVC), the 720 cm^{-1} peak is due to the ring deformation of substituted aromatic structure. The incorporation of the PY moiety in the PNVC chain is endorsed by the above data.
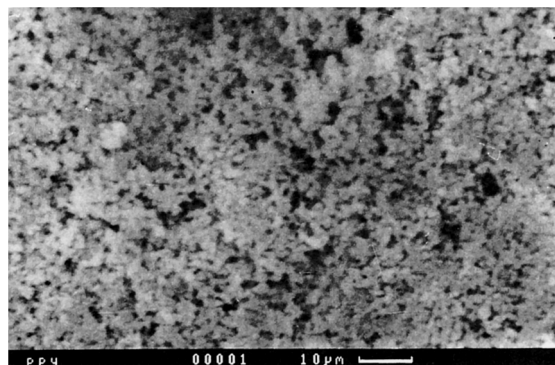
(i)
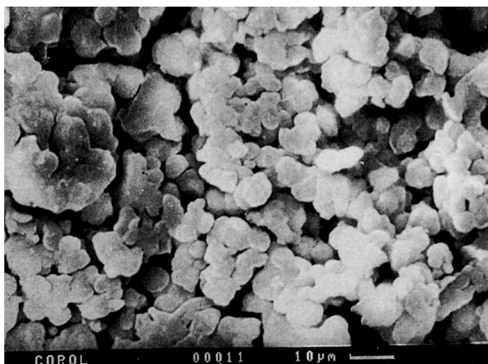
(ii)
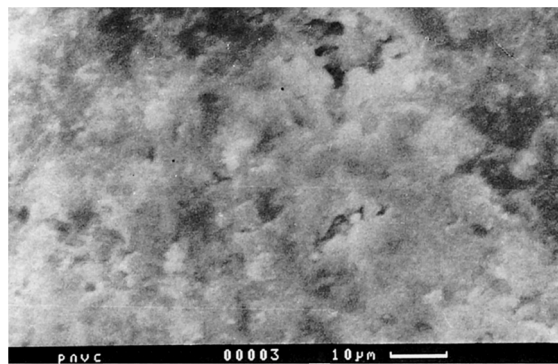
(iii)

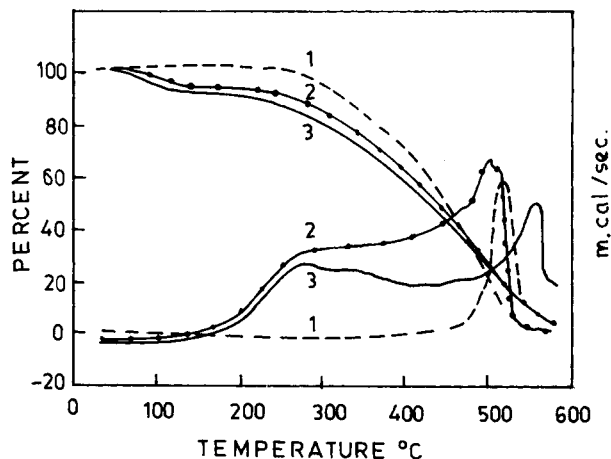**Figure 1** Scanning electron micrographs of (i) PPY, (ii) P(PY–NVC), and (iii) PNVC.

Figure 2 TGA and DSC curves of (1) PNVC, (2) P(PY–NVC), and (3) PPY.

Morphology

SEM photographs (Fig. 1) reveal that PPY shows close-packed agglomerates of irregular size and shape and appears to be characterized by a porous spongelike structure. In contrast, PNVC possesses densely packed agglomerates in which particles are more minutely dispersed; for P(PY–NVC), the SEM is markedly distinct from those of PPY and PNVC and shows a large globular particle formation.

Thermal Stability

Figure 2 indicates that the thermal stability of P(PY–NVC) is intermediate between those of PNVC and PPY, respectively. The trend in T_i, the initial decomposition temperature, is PPY (210°C) < P(PY–NVC) (225°C) < PNVC (255°C) (hymp) and another at 510°C, for P(PY–NVC). The DSC scan for PPY is similar but the peaks
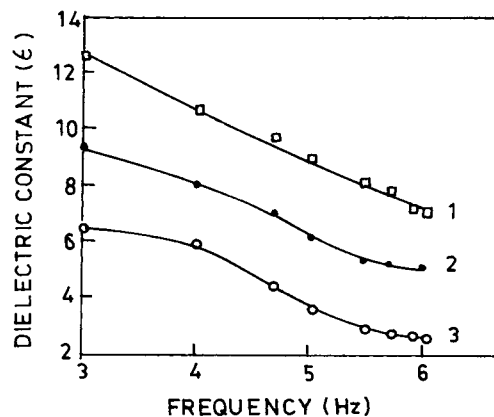

Figure 3 Dielectric constant vs. frequency plots for (1) PPY, (2) P(PY–NVC), and (3) PNVC.
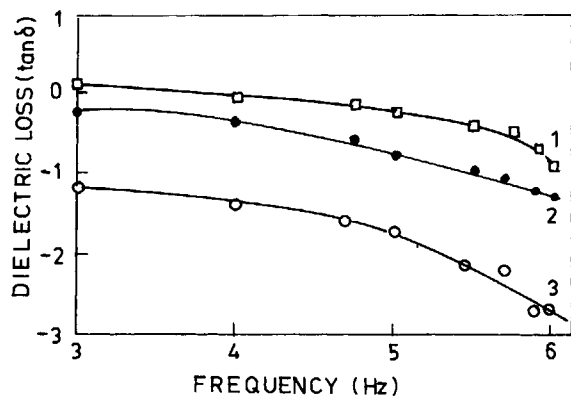
Figure 4 Dielectric loss vs. frequency plots for (1) PPY, (2) P(PY–NVC), and (3) PNVC.

are less sharp. It is obvious from the DSC scan that major structural degradation occurs in the range 250–520°C in these systems.

Dielectric Characteristics

Figure 3 indicates that the dielectric constant (γ) and loss (tan δ) for PPY, PNVC, and P(PY–NVC) exhibit a monotonic fall with the applied frequency to a limiting value. At a frequency of 1 kHz, the dielectric constant trend is PPY (12.61) > P(PY–NVC) (9.4) > PNVC (6.5). The tan δ frequency trend is indicative of a broad relaxation in all the three systems (Fig. 4).

The general trend observed in these systems is similar to that exhibited by other N-bearing polymer systems. However, copolymerization of NVC with PY does not possibly result in a highly conjugated structure which is evident from the lower dielectric constant, as compared to PPY at a particular frequency due to a lower extent of dielectric polarization.

Conductivity

Table I represents the conductivity characteristics of PPY, PNVC, and P(PY–NVC) prepared under the present and other reaction conditions. Interestingly, the specific conductivity of P(PY–NVC) prepared in an aqueous suspension falls in the range $(2.2–3.5) \times 10^{-3}$ S cm^{-1}. This value is 10^3 times higher than the conductivities of P(PY–NVC) reportedly achieved in ether–FeCl$_3$ $(3.7 \times 10^{-6}$ S cm$^{-1})$- or toluene o-chloranil $(3.6 \times 10^{-6}$ S cm$^{-1})$-initiated copolymerization[2] of PY and NVC. To the extent that we have conducted the literature survey, this appears to be the highest ever reported conductivity for PY–NVC-based copolymer systems. Even a blend[9] of PPY and PNVC obtained with FeCl$_3$ (THF) reportedly exhibits a conductivity in the order 3.3×10^{-6} S cm^{-1}. In this background, the

results of the present investigation should be expected to have considerable significance. Water has been recognized[3,4,10] as one of the major parameters in conductive PPY and PNVC syntheses. This observation is fully consistent with our recently reported results[11-12] on the improvement of conductivity of PNVC and PPY prepared in aqueous suspension. As to the conductivity enhancement behavior of the water–FeCl$_3$ system in regard to PY, NVC, and PY + NVC polymerization, several factors such as the relative extent of incorporation of NVC and PY moieties in P(PY–NVC) FeCl$_3$ solvation, dielectric constant, medium basicity, and possible changes in doping processes may be responsible as recognized by other workers in the field.[13] As of now, the exact mechanism by which such effects influence the present system remains open. Further studies in these directions are in progress.

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