

Conductivity, thermal stability, dielectric and morphological characteristics of poly(*N*-vinylcarbazole) prepared in aqueous suspension

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Suspension polymerization of *N*-vinylcarbazole in toluene/water solvent induced by FeCl₃ in varying mole ratios with the monomer, yields a polymer with appreciably higher specific conductivity ($\sim 1 \times 10^{-4} \text{ S cm}^{-1}$) than that of a conventionally prepared poly(*N*-vinylcarbazole) (PNVC). Thermal stability, morphology and dielectric characteristics of suspension-polymerized PNVC have also been studied.

(Keywords: suspension polymerization; conductivity; thermal stability; dielectric; morphology)

Introduction

Among the *N*-heterocyclics, poly(*N*-vinylcarbazole) (PNVC) has enjoyed overwhelming research attention in view of the remarkable photophysical properties of the polymer¹⁻⁴. As regards electrical conductivity, PNVC obtained by conventional methods is essentially an insulator^{2,3} ($\sim 10^{-10}$ – $10^{-16} \text{ S cm}^{-1}$). We report here that PNVC, when prepared by FeCl₃ in aqueous suspension, develops appreciably enhanced conductivity. While there is much literature on the role of water in the preparation of conductive polypyrrole⁵⁻⁷, the suspension polymerization of *N*-vinylcarbazole (NVC) in a biphasic system using FeCl₃ has not, to our knowledge, been explored to date in producing PNVC with improved conductivity. The variation of other bulk properties such as thermal stability, morphology and the dielectric constant of the suspension-polymerized PNVC in relation to those of a conventionally prepared PNVC are also highlighted.

Experimental

Materials. *N*-vinylcarbazole (BASF, Germany) was recrystallized from *n*-hexane (BDH) and kept in the dark. Anhydrous ferric chloride (Fluka) was used as such. Once-distilled water was redistilled over alkaline permanganate. All solvents used were AR grade materials and were purified prior to use by recommended procedures.

Polymerization. In view of the insolubility of NVC in water, the suspension polymerization of this monomer was performed in a biphasic system. A calculated quantity of NVC was dissolved in a known minimum volume of toluene and the solution was added to water containing the desired amount of FeCl₃. The mixture was continuously stirred under nitrogen atmosphere. Gradually, the toluene layer separated out as globules containing the polymer. The PNVC was precipitated in methanol, filtered and repeatedly washed with methanol to remove unreacted monomer. The polymers were dried in vacuum at 60°C for 6 h.

Characterization. The intrinsic viscosity of the polymers was determined by an Ostwald viscometer in benzene at 27°C. The i.r. spectra were recorded on a Perkin Elmer 883 i.r. spectrophotometer in KBr pellets. Thermogravimetry and differential scanning calorimetry were performed on a Stanton-Redcroft STA 625 instrument. Scanning electron micrographs were taken by a CAM SCAN series 2DV. X-ray diffractograms of the powdered samples were taken on a Philips PW/1710/00 model with CuK α radiation. Dielectric constants and the loss ($\tan \delta$) factors were recorded at different frequencies on a HIOKI 3530 LCR Hitester instrument with silver-coated pellets of PNVC. The pellets were prepared under 5.1–6.1 t pressure. Electrical conductivity measurements were performed on a Keithley 617 solid state electrometer.

Results and discussion

General features of polymerization. Table 1 presents some typical polymerization data for NVC. The polymerization is evidently sensitive to the relative amount of FeCl₃, time and nature of the medium. Under the experimental conditions cited in Table 1 the conversion seems to level off at about 60% beyond a FeCl₃:NVC mole ratio of 9:1.

PNVC was recovered as a light-brown powder in contrast to polypyrroles which are reportedly^{7,8} isolated as intensely black powders. The formation of deep-black polypyrroles during oxidative polymerization is typical of charge-transfer reaction through the *N*-heteroatom. Significantly, although charge-transfer polymerization of NVC in the presence of oxidants is extremely facile⁹, the conventional cationic initiation by Lewis acids through vinylic double bonds has been endorsed in earlier studies by Biswas *et al.*^{10,11}. Any eventual hydrolysis of FeCl₃ in aqueous medium forming HCl will also lead to cationic initiation as reported by Biswas⁴.

Morphology. Figure 1 presents four scanning electron micrographs of PNVC prepared with different FeCl₃:NVC mole ratios. In general, these reflect densely packed agglomerates in which the particles are more minutely dispersed in the case of the PNVC prepared with a higher mole ratio of FeCl₃:NVC. In contrast, the micrograph

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Table 1 Polymerization^a and conductivity data for PNVC^b prepared in aqueous suspension at ambient temperature

Run no.	Reaction condition		Polymerization time (h)	Conversion (%)	$[\eta]$ (dl g ⁻¹)	Conductivity (S cm ⁻¹)
	Mole ratio of FeCl ₃ :NVC	Solvent ^c				
1	1:1	Aqueous suspension	6	28	0.01	9.3×10^{-6} 8.7×10^{-6c}
2	3:1	Aqueous suspension	6	32	0.017	2.4×10^{-5} 2.0×10^{-5c}
3	6:1	Aqueous suspension	6	38	0.03	6.98×10^{-5}
4	9:1	Aqueous suspension	6	42	0.05	9.14×10^{-5}
5	12:1	Aqueous suspension	6	61	0.10	1.01×10^{-4}
6	15:1	Aqueous suspension	6	61	0.12	9.83×10^{-5}
7	6:1	Aqueous suspension	10	42	–	–
8	9:1	Aqueous suspension	10	60	–	–
9	0.127:1	Ether	2	78	0.01	1.83×10^{-10}
10	2.25:1	Ether	2	79	–	2.9×10^{-8}
11	Lewis acid (AlCl ₃ , AsCl ₃)	Benzene	0.5	45	–	4.2×10^{-16}

^aIn runs 1–8, total reaction volume was 100 ml (2 ml toluene + 98 ml water)

^bPNVC obtained in runs 1–8 was light brown in colour and in runs 9–11, white; it was freely soluble in all common solvents for PNVC

^cDuplicate experimental values

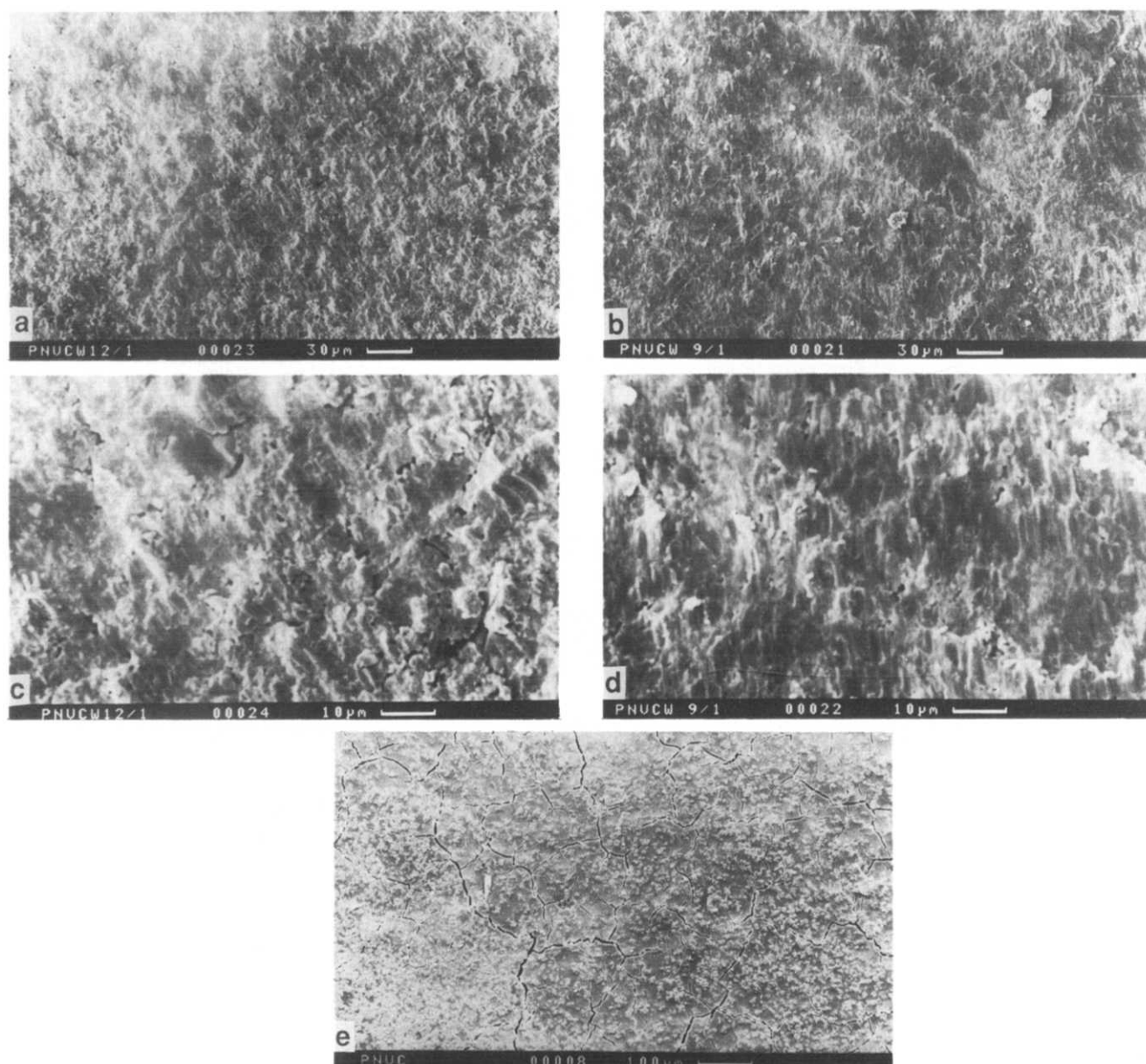


Figure 1 Scanning electron micrographs of PNVC prepared with FeCl₃:NVC mole ratios: (a), (c) 12:1; (b), (d) 9:1; and (e) in ether

of a PNVC prepared in ether (Figure 1e) appears to lack the densely packed arrangement.

X-ray diffraction. X-ray diffraction patterns of PNVC obtained with FeCl_3 :NVC mole ratios of 6:1 and 9:1 were analysed and compared with those obtained in ether. The data presented in Table 2 indicate that suspension-polymerized PNVC exhibits some crystalline pattern, the per cent crystallinity tending to increase with increasing FeCl_3 :NVC mole ratio used during the polymerization. The appearance of additional peaks further endorses the later contention. Another feature of significance is that, compared to PNVC in ether, PNVC produced in aqueous suspension exhibits higher 2θ peaks; this implies a decrease in the interplanar distance which may favour conduction processes, as observed.

Thermal stability. Thermogravimetric analysis reveals that PNVC prepared with FeCl_3 :NVC mole ratio of 9:1 exhibits higher stability than that obtained with a ratio of 6:1. The temperatures for initial, 20%, 40% and 60% decomposition for these two polymers are respectively 230, 190; 310, 280; 420, 370; and 460, 420°C. In either case, the polymers undergo 95% decomposition at $>550^\circ\text{C}$. The higher stability of the 9:1 PNVC is evidently due to a higher molecular weight than the 6:1 PNVC (Table 1). The FeCl_3 (ether) initiated PNVC, on the other hand, exhibits a somewhat higher initial decomposition temperature, about 260°C , but beyond 20% decomposition (320°C) becomes progressively less stable (40% at 350°C and 50% at 390°C) than the suspension-polymerized PNVC. The trend is again consistent with the lower molecular weight for this polymer. Differential thermal analysis reveals a sharp exotherm around 450°C , signifying oxidative degradation of the polymer network.

Dielectric characteristics. Figure 2 represents the variation of the dielectric constant (ϵ) and the dielectric loss factor ($\tan \delta$) with the applied frequency for PNVC prepared with various FeCl_3 :NVC mole ratios in water suspension. It appears that the trend is best described by a single curve passing through a mean point which is almost an average of all points at a particular frequency corresponding to six sets of PNVC. This evidently implies that increasing the mole content of FeCl_3 does not have any perceptible effect on the dielectric property. The monotonic fall in the dielectric constant and loss curve with applied frequency has been observed before with N-bearing heterocyclic polymer systems and signifies a broad relaxation process¹². Further, PNVC prepared with a Lewis acid in benzene¹³ also exhibits a dielectric constant of 4.89–4.63 in the frequency range 10^3 – 10^5 Hz, which is comparable to that observed in the present system.

Table 2 X-ray diffraction characteristics of PNVC produced in toluene/water/ FeCl_3 system

Run no. in Table 1	Major crystalline peaks, 2θ (deg)	Crystallinity (%)
3	6.4, 10.4, 11.6, 14.2, 21.4, 23	20.6
4	6.4, 11.6, 13.7, 14.4, 18.5, 21.3, 23	25.8
9	6.9, 9.7, 11.5, 13.4	21.9

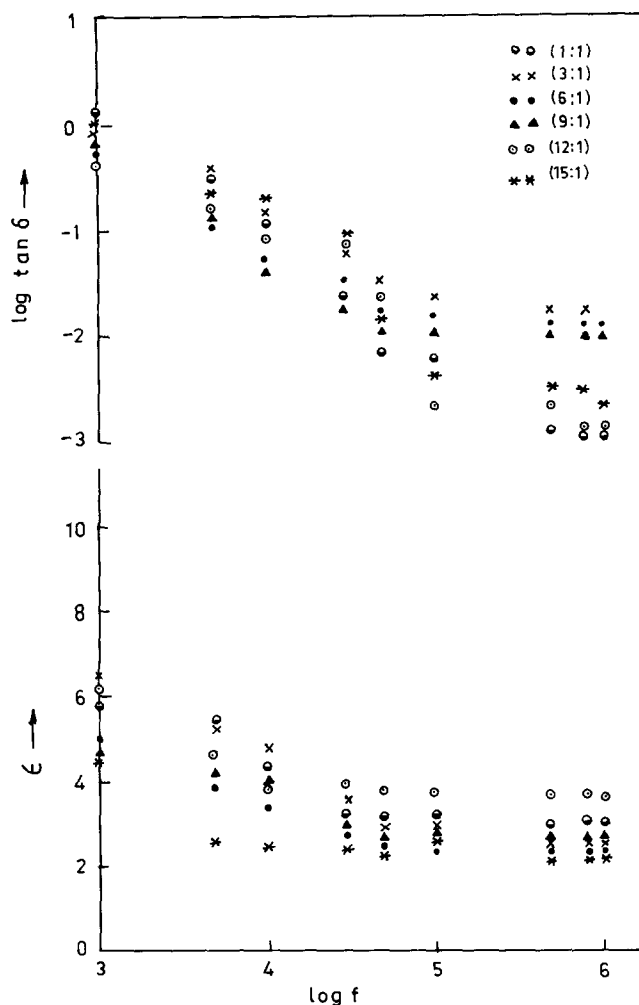


Figure 2 Dependence of dielectric constant (lower graph) and dielectric loss factor (upper graph) of PNVC on applied frequency

Conductivity characteristics. Data presented in Table 1 clearly reveal that the specific conductivity values of suspension-polymerized PNVC are considerably improved relative to the FeCl_3 -ether initiated PNVC and even more so compared to a Lewis acid initiated PNVC. In fact, it is significant that PNVC can be prepared by such a simple procedure to yield specific conductivity as high as $\sim 10^{-4} \text{ S cm}^{-1}$ which, to our knowledge, has not been reported to date. The above data further reveal that with the experimental conditions used, a limiting conductivity value of $1 \times 10^{-4} \text{ S cm}^{-1}$ is reached above a FeCl_3 :NVC mole ratio of 9:1. Evidently, other experimental parameters need to be examined to establish the highest attainable conductivity values in these systems.

It is relevant to point out that solvent, particularly water, has been recognized⁵⁻⁷ as one of the major parameters in conductive polypyrrole preparations. Myers⁷ pointed out that during the course of FeCl_3 /pyrrole reaction, significant changes in the doping process *vis-à-vis* the nature of the dopant species are possible, which lead to enhanced conductivity. Morphological and/or molecular weight changes are other important factors in this context. The remarkable increase in the specific conductivity of PNVC as observed in this context appears to be consistent with the above theory.

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