Characterization of Copolymers of N-Vinyl-2-Pyrrolidone with 2-Phenyl-1,1-Dicyanoethene

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Synopsis

Copolymers of N-vinyl-2-pyrrolidone and 2-phenyl-1,1-dicyanoethene were studied. Infrared, proton, and carbon-13 spectra of the copolymers are discussed by comparison with poly(N-vinyl-2-pyrrolidone), model compounds, and various copolymers. Thermal behavior of the copolymers was investigated by using DSC, TMA, and TGA methods. Thermal as well as thermooxidative stability of the copolymers was found to be lower than those of poly(N-vinyl-2-pyrrolidone).

INTRODUCTION

In the preceding article[1] an investigation on the copolymerization of N-vinyl-2-pyrrolidone (NVP) with 2-phenyl-1,1-dicyanoethene (PDE) was reported.

The present work deals with the characterization of the NVP–PDE copolymers, which were found to be predominantly alternating ones, where $n = 1$ and $m \geq 1$:

$$(-CH-\underset{\underset{CN}{|}}{\overset{\overset{CN}{|}}{C}}-)_n(-CH_2-CH-)_m$$
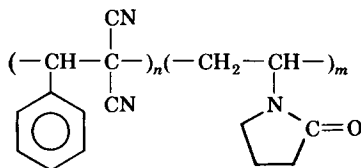
EXPERIMENTAL

Preparation of Copolymers

The copolymer samples for characterization were prepared in benzene at 70°C using 0.0045 mol/L of AIBN as initiator and 60 mol % of NVP in the monomer feed at 2 mol/L total monomer concentration. The copolymer sample for NMR analysis was obtained in carbon tetrachloride at NVP/PDE = 3/1 (mol), [AIBN] = 0.045 mol/L, [NVP + PDE] = 2 mol/L. 1-Dodecanethiol (0.032 mol/L) was used as a chain modifier. The crude copolymers precipitated in methanol were filtered by suction using sintered glass crucibles. The copolymers were washed repeatedly and dried in a vacuum oven at 70°C for 100 h.

Microanalysis of the copolymer samples was performed by Galbraith Laboratories. C, H, and N contents were measured as appropriate, and O contents calculated as necessary. The copolymers composition was estimated based on elemental and moisture analysis.

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Moisture analysis of the copolymers was done using a Mitsubishi moisture meter, Model CA-05 with precision $\pm$ 3 μg for 10 mg sample.

Infrared Spectra

An IBM Model FT-IR-32 spectrometer was used with a resolution of 4 cm^{-1} and an accumulation of 40 scans. The absorption mode was used on finely powdered samples prepared as KBr discs.

NMR of Copolymers

The proton noise-decoupled carbon-13 NMR spectra were obtained on a Bruker WH-270 Fourier transform spectrometer operating at 67.88 MHz. Frequency stabilization was obtained by deuterium lock. Tetramethylsilane (TMS) was used as an internal standard, and all chemical shifts are reported downfield from TMS. Both carbon-13 and proton NMR spectra of the NVP–PDE copolymers were taken in DMSO-d$_6$ solution at ambient temperature.

X-Ray Analysis

X-ray diffractogram was recorded with a Laue camera mounted on a Norelco generator operating at 35 kV and 35 mA using Ni-filtered Cu-Kα radiation with sample to film distances of 3–7 cm.

Thermal Analyses

DSC analysis was performed using a DuPont 9900 thermal analyzer with 910 DSC module. A sample of 10–15 mg was crimped in an aluminum pan and then heated at a 10°C/min rate. The atmosphere employed was air or nitrogen.

A DuPont 943 thermomechanical analyzer (TMA) was used in the penetration mode. A copolymer sample was pressed into about 1 mm thick disc (5 mm diameter) and heated with 5°C/min rate under 50 g load.

Thermogravimetric analyses (TGA) were performed in a stream of nitrogen or air at 50 mL/min by using a DuPont 951 thermogravimetric analyzer. The heating rate was 10°C/min and the sample size was 5–15 mg of polymer.

RESULTS AND DISCUSSION

NVP–PDE copolymers are white, fine powders. Wide-angle X-ray diffraction analysis of powder copolymer sample demonstrated diffuse amorphous pattern. The copolymers of different composition were found insoluble in alcohols, diols, ketones, DMF, methylene chloride, and acetonitrile and partly soluble in DMSO and chloroform. Poor solubility of the copolymers apparently associated with strong intermolecular interactions due to the highly polar nature of the substituents. Moreover, the proximity of the bulky side groups prevents the solvent molecules from gaining access to the backbone. Furthermore, NVP–PDE copolymers are hygroscopic and difficult to dry. Copolymers dried for more than 100 h at 120°C in vacuum (1 mm Hg) still contained ca. 1% of water as evaluated by Karl Fisher analysis. The presence
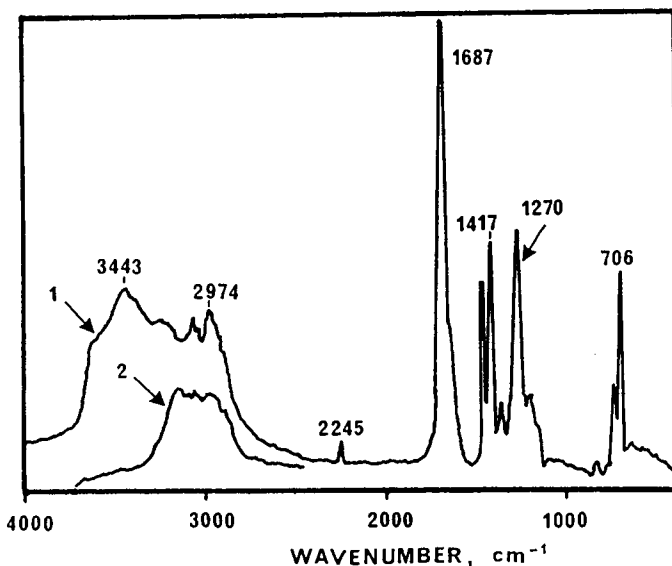
Fig. 1. FT-IR spectrum of the NVP–PDE copolymer: (1) the copolymer dried at 70°C for 100 h in vacuum; (2) the copolymer dried at 120°C for 100 h in vacuum.

of bound water results in high degree inter- and intramolecular hydrogen bonding similar to one observed in poly(N-vinyl-2-pyrrolidone) (PNVP).[2]

IR Spectrum

The IR absorption spectrum of the NVP–PDE copolymer (Fig. 1) demonstrated characteristic bands for both PDE and NVP monomer units. The assignment of the band in the 3400 cm^{-1} region to bound water was made according to similar absorption in the spectrum of PNVP.[3] This band significantly decreases in intensity on heating. Other bands include C—H stretch vibrations at 3100–2800 cm^{-1} and a PDE nitrile group stretch band at 2245 cm^{-1}. Carbonyl amide band occurs as a strong peak near 1690 cm^{-1} close to the frequency observed in the spectrum of PNVP.[2] Methylene deformation peaks in the 1500–1400 cm^{-1} region have the same pattern as in the spectrum of PNVP.[3] The band 1270 cm^{-1} represents C—N stretching mode of NVP monomer unit whereas the doublet at 740–706 cm^{-1} is characteristic of out-of-plane C—H bending absorption of monosubstituted PDE aromatic ring.

Proton NMR Spectrum

The 270 MHz solution proton NMR spectrum of NVP–PDE copolymer (60 mol % NVP content) is shown in Figure 2. The observed absorptions were tentatively assigned based on comparison with the spectra of the monomers and their copolymers as well as PNVP. The spectrum shows a broad signal of aromatic protons at 8.1–6.8 ppm which result from overlapping multiplets of the five spin system. The resonance in the region 5.5–4.3 ppm was assigned to the NVP methine proton in NVP–PDE dyads or NVP-centered triads
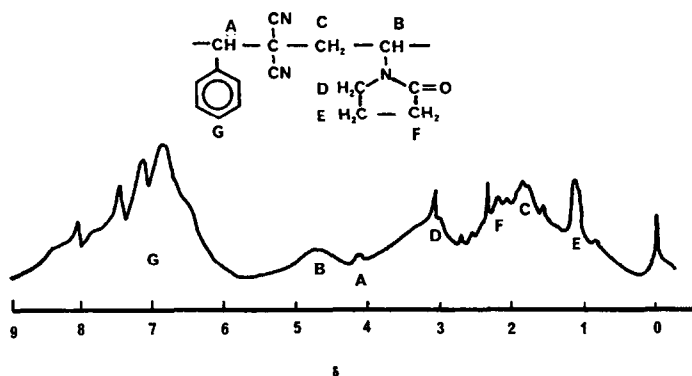
Fig. 2. Proton NMR spectrum of NVP–PDE copolymer with 60 mol % NVP content in DMSO-d_6.

PDE–NVP–PDE. The methine proton is more subject to deshielding than the corresponding one in PNVP, where it appears as absorption at 3.6 ppm.[4] This observation leads to a suggestion that deshielding of the NVP methine proton might be associated with high content of NVP dyads of type I and small contribution of dyads of type II:

(I)   (II)
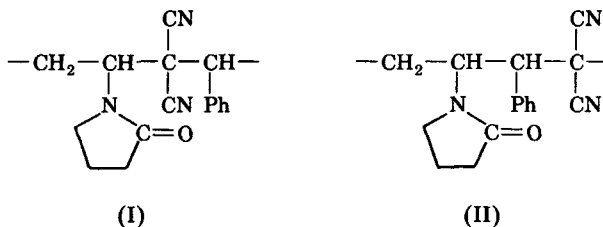
The broadness of the methine band is also indicative of different environmental effects of neighboring units. The deshielding conceivably arises from a powerful electron withdrawal by the neighboring dicyano groups when the NVP unit is sandwiched between PDE units in the copolymer chain. Analogous influence of the electrophilic monomer unit environment on the methine proton resonance position of the donor monomer unit was observed in the case of alternating copolymers of vinyl acetate with PDE[5] and ethyl 3-phenyl-2-cyanopropenoate.[6] Thus the methine proton of the vinyl acetate unit in these copolymers had resonance at 5.3 ppm whereas in the spectrum of poly(vinyl acetate) it absorbs upfield at 4.5 ppm. The signal at 4.1 ppm can be assigned to methine resonance of the PDE unit which absorbs in this region in the spectrum of PDE–vinyl acetate copolymer.[5] The broad absorption in the 4.0–2.7 ppm region with maximum at 3.2 ppm corresponds to the resonance of methylene protons of the carbon close to the nitrogen atom of the NVP lactam ring. This assignment is based on the comparison with the spectrum of PNVP. The overlapping peaks in the 2.7–0.3 ppm region are assigned to the resonance signals of lactam and backbone methylene protons of NVP on the

basis of integration data and the order of absorption in PNVP.[4] The composition of the NVP–PDE copolymers can be estimated from proton NMR spectra using the relation $m_1/m_2 = (S_2 - 0.2S_1)/1.8S_1$, where m_1 and m_2 are mole fractions of NVP and PDE in the copolymer, respectively, S_1 is the area of the peak corresponding to the absorption of PDE aromatic protons, and S_2 is the peak area of all other protons of PDE and NVP units.

Carbon-13 NMR

The 67.88 MHz solution carbon-13 NMR spectrum of NVP–PDE copolymer (60 mol % NVP content) is shown in Figure 3. The tentative peak assignments were made by analogy to the spectra of model compounds and polymers. The well resolved carbon resonance at 17 ppm easily can be assigned to the methylene carbon in the lactam ring as in the spectrum of PNVP.[7] Following the analogy, peaks at 30 and 36 ppm were assigned to another methylene carbon of the lactam ring and NVP methylene backbone carbon, respectively. The resonance in the 39–45 ppm range evidently corresponds to the overlapping absorptions of NVP methylene carbon CH_2N and PDE carbon with geminal cyano groups. The methylene carbon in PNVP has chemical shift values at 42–44 ppm,[7] whereas the signal at 41 ppm is characteristic of dicyanosubstituted carbon in the spectra of model compound 4, 4-dicyano-3, 5-diphenylcyclohexanone[8] and PDE–vinyl acetate copolymer.[5] The assignment of the broad absorption at 45–55 ppm to the resonances of benzylic carbon of PDE and methene carbon of NVP monomer unit is made according to the values reported for PNVP, model compounds, and PDE copolymers.[5,7,8] The carbons of the two nitrile groups evidently absorb at 115 ppm as in polyacrylonitrile[9] and PDE, whereas the peak at 120–135 ppm belongs to the carbon resonance of the PDE phenyl group. The peak at 176 ppm can be easily assigned to the carbonyl carbon in NVP monomer unit.[10]
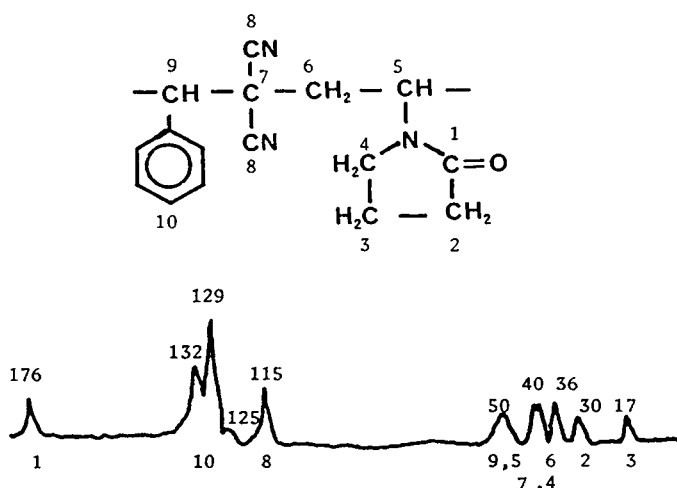

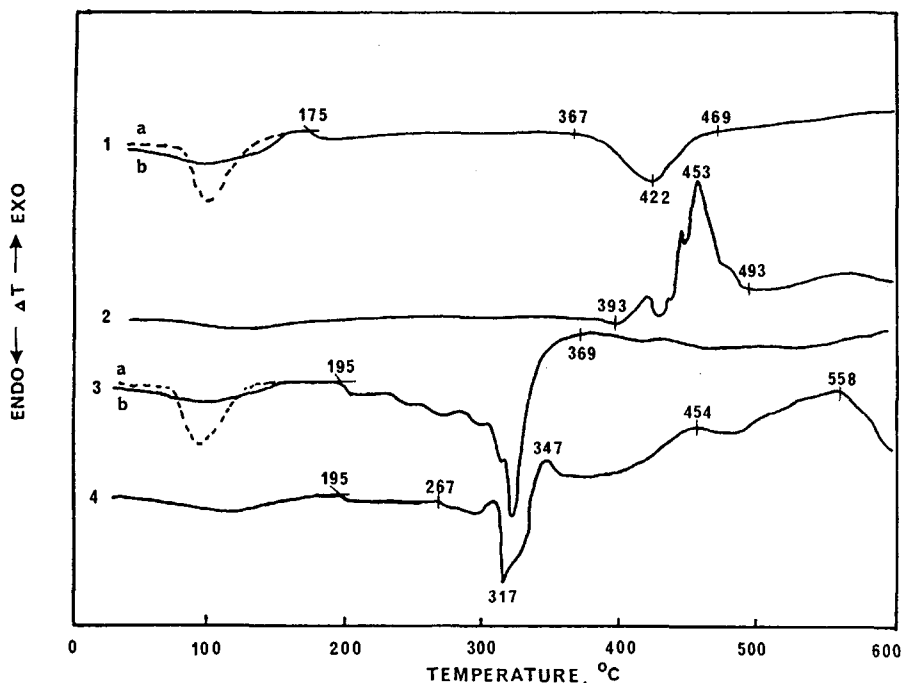Fig. 3. Carbon-13 NMR spectrum of NVP–PDE copolymer in DMSO-d_6.

Fig. 4. DSC traces of PNVP and NVP–PDE copolymer heated in air and nitrogen: (1a, b) PNVP dried at 70 and 120°C, respectively, heated in N_2; (2) PNVP heated in air; (3a, b) NVP–PDE copolymer dried at 70 and 120°C, respectively, heated in N_2; (4) NVP–PDE copolymer heated in air.

Thermal Behavior

The thermal properties of NVP–PDE copolymers as well as PNVP were studied by DSC, TGA, and TMA. Typical DSC results are shown in Figure 4 in both air and nitrogen. Substantial effects due to the water content were observed for PNVP and NVP–PDE copolymer dried in vacuum at 70°C. Large endotherms (curves 1a and 3a) presumably due to volatilization of water were detected between about 45 and 150°C. The effects of drying the samples (100 h at 120°C in a vacuum oven) are shown in traces 1b, 2, 3b and 4 of Figure 4, where removal of water is indicated by the weak volatilization endotherms. The areas of these endotherms correlated well with total water content estimated by the Karl Fisher method. DSC traces of the NVP–PDE copolymer heated in nitrogen and air demonstrate glass transition at 195°C. T_g of PNVP was observed at 175°C, which agreed well with literature values.[4] To eliminate the plasticization effect of moisture, the samples were heated to about 20°C greater than T_g and then cooled. Glass transition temperatures were determined from the thermogram on the third recycle run. The higher T_g of the copolymer as compared to that of PNVP can be explained by steric crowding and polar interactions. It was found that the planarity of phenyl and pyrrolidone side groups severly limits the conformations available to the pair of backbone bonds flanked by the side groups.[11] In addition to being planar, the side groups of NVP are highly polar, because of the incorporation

TABLE I
Decomposition Data of NVP–PDE Copolymer and PNVP

	Temperature (°C)					
	Air			Nitrogen		
Sample	Onset	10% wt loss	50% wt loss	Onset	10% wt loss	50% wt loss
NVP–PDE copolymer	260	350	350	260	317	350
PNVP	320	410	450	336	415	450

of a peptide bond in the five-membered pyrrolidone ring. Interactions between polar peptide and cyano groups in neighboring units significantly limit the mobility of the macrochain. The information on degradation of the copolymers and PNVP was obtained from DSC and TG analysis. The products of decomposition were not analyzed in this study and the mechanism remains to be investigated. Results of the analyses are summarized in Table I.

DSC traces of the copolymer heated both in air and nitrogen have similar decomposition endotherms with maximum at 314°C. Heating the copolymer in air above this temperature results in thermooxidative degradation as evidenced by three exotherms. Thermal and thermooxidative decomposition of PNVP starts at much higher temperatures with endotherm in the 325–500°C range when heated in air. Figure 5 shows TGA curves for the thermal degradation of the copolymer with 60 mol % of NVP content and PNVP in both air and nitrogen. It can be seen that, for both types of atmospheres, the
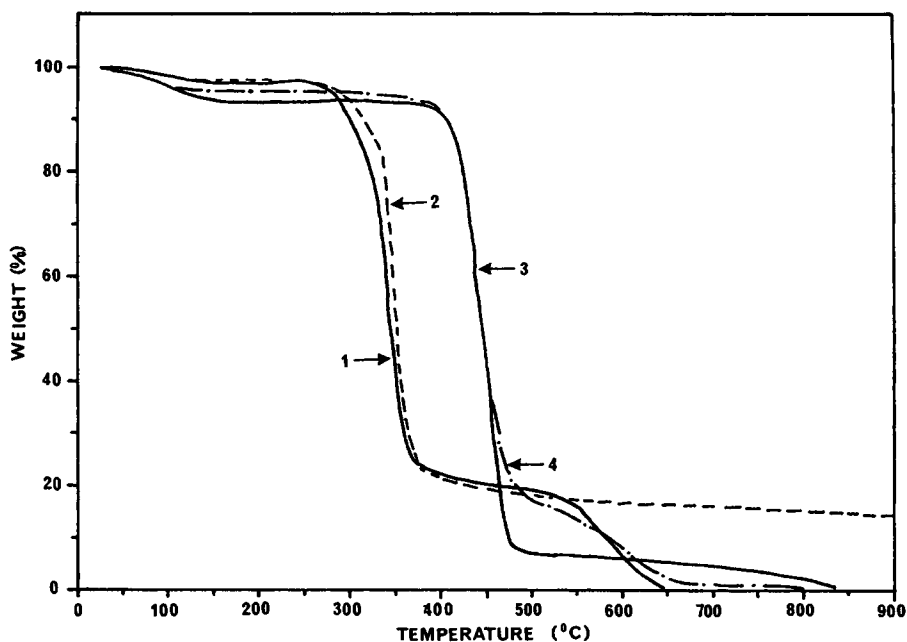

Fig. 5. Results of TG analysis: (1, 2) NVP–PDE copolymer heated in air and nitrogen, respectively; (3, 4) PNVP heated in air and nitrogen, respectively.
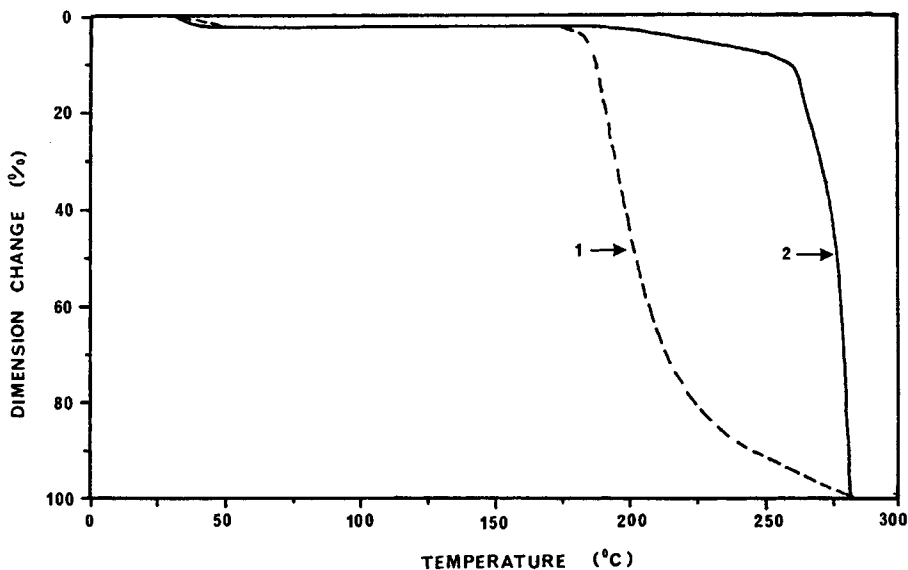
Fig. 6. TMA traces of PNVP and NVP–PDE copolymer: (1) PNVP; (2) NVP–PDE copolymer.

copolymer after devolatization of water began to degrade at about 275°C. However, in nitrogen, the reaction was complete at about 370°C at 80% conversion. The decomposition in air occurred in two distinct stages, rapidly in the 260–400°C region, then more slowly at 500–700°C. The formation of thermally stable carbon residue upon decomposition of NVP–PDE copolymer in nitrogen apparently is associated with cyclization and crosslinking reactions involving cyano and cyclic amide groups. In air, however, as the volatile degradation products are formed, some combustion takes place, resulting in the exotherms seen in DSC (Fig. 4). TGA traces of PNVP heated in air showed the same two-stage degradation pattern as for the copolymer. Heating PNVP in nitrogen resulted in degradation with 95% conversion below 500°C with very slow decomposition of the residual polymer to 900°C with about 1% of carbon residue left at this temperature.

Figure 6 shows TMA penetration traces at a programmed heating rate of 5°C/min. PNVP and NVP–PDE copolymer began to soften at 175 and 193°C, respectively, which corresponded well to glass transition temperatures observed on DSC scans. Full penetration in the case of PNVP was achieved below 250°C whereas NVP–PDE copolymer remained very rigid until the onset of degradation at about 260°C. NVP–PDE copolymers, similarly to polyacrylonitrile and like many other high-nitrile polymers, degrade thermally below their softening point.

The results of DSC, TG, and TM analyses show that NVP–PDE copolymers have significantly lower thermal and thermooxidative stability than PNVP. This is likely due to the presence of quaternary carbon, which weakens the adjacent C—C bond and thermally sensitive methene group of PDE unit.

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