Polymer Bulletin 12, 65–70 (1984)

Polymer Bulletin

Copolymerization of Methyl-α-Cyanocinnamate with N-Vinyl Pyrrolidone

G. B. Kharas* and M. H. Litt

Department of Macromolecular Science Case Western Reserve University Cleveland, OH 44106, USA

*) To whom correspondence should be addressed. Present address: Albany International Corp. Membrane Development Venture 921 Providence Highway Norwood, MA 02062 USA

SUMMARY

N-vinyl pyrrolidone was copolymerized with methyl α-cyanocinnamate in solution by radical initiation at 70°C up to low conversions. Essentially equimolar copolymers were formed over a wide range of monomer feed ratios. Terminal, penultimate, and complex copolymerization models were applied by using the copolymer composition data. The participation of monomer complexes in the propagation reactions could account for the deviations of the copolymerization behavior from terminal and penultimate models. The copolymers were characterized by IR, PMR and carbon-13 NMR spectroscopy.

INTRODUCTION

Electron-deficient trisubstituted olefins carrying cyano and carboalkoxy substituents copolymerize readily with monosubstituted electron-rich monomers under free radical conditions leading to random (BORROWS *et al*, 1955, KRIESEL *et al*, 1964, HALL *et al*, 1977) and alternating (KHARAS *et al*, 1983) copolymers. The steric hindrance due to the β-substituent of the olefin is counteracted by the favorable electronic effects of two α-substituents in the stabilization of the intermediate radical. Donor-acceptor complexation between electrophilic trisubstituted ethylenes and donor monomers was noted in some cases (HALL *et al*, 1975).

The present study was undertaken to gain more information on copolymerization behavior of trisubstituted ethylenes with cyano and carboalkoxy substituents.

EXPERIMENTAL

Methyl α-cyanocinnamate was prepared in 90% yield by the method of CARSON (1928). The monomer structure was identified by IR and NMR and proved that the ester did not contain Z-isomer (HAYASHI,1966). N-vinyl pyrrolidone was distilled in vacuum at 65°C/1mm Hg before use. The copolymerization procedure was described earlier (KHARAS *et al*, 1983). The copolymers were prepared at predetermined ratios of monomer feed using 0.0045 mole/liter of AIBN at an overall monomer concentration 2 mole/liter in 20 ml of chloroform. The copolymerization was conducted at 70 ± 0.5°C and stopped at low conversion by freezing the ampules in liquid nitrogen; the frozen solutions were then quickly melted and diluted with chloroform. The crude copolymers were precipitated in a large excess of ethyl ether and purified by precipitation from chloroform solution into an excess of ethyl ether. The copolymers were dried under reduced pressure at ambient temperature. IR spectra were recorded on KBr pellets containing about 1% by weight of the pulverized sample using a Digilab FTS-14 Infrared Spectrometer. PMR spectra of comonomer mixtures and copolymer solutions in $CDCl_3$ were obtained on Varian T-60 spectrometer. Measurements were performed at 30°C with TMS as internal standard. Carbon-13 NMR spectrum of the copolymer solution in $CDCl_3$ was recorded on the Varian XL-100 spectrometer.

RESULTS AND DISCUSSION

Methyl α-cyanocinnamate (MCC) does not homopolymerize by radical initiation like other electron-deficient trisubstituted ethylenes with cyano and carboalkoxy substituents, but copolymerizes readily with N-vinyl pyrrolidone (NVP). The composition of the MCC-NVP copolymers was determined from PMR spectra using the relation: $m_1/m_2 = 1.8\ S_1/S_2 - 0.8S_1$, where m_1 and m_2 are molar fractions of M_1(NVP) and M_2(MCC) monomer units in the copolymer, respectively; S_1 is the area of the peak corresponding to the absorption of MCC aromatic protons, S_2 is the peaks area of all other protons (MCC and NVP).

The data on the composition of the copolymers obtained at low conversions against the feed composition is presented in Table 1.

TABLE 1 Copolymerization of NVP (M_1) and MCC (M_2)

FEED COMPOSITION					COPOLYMER COMPOSITION	
Loaded		Calculated*)				
mole/l		mole/l			mole fraction	
$[M_1]$	$[M_2]$	$[M_1]$	$[M_2]$	[C]	m_1	m_2
1.8	0.2	1.782	0.182	0.018	0.567	0.433
1.6	0.4	1.568	0.368	0.032	0.535	0.465
1.4	0.6	1.358	0.558	0.042	0.522	0.478
1.2	0.8	1.152	0.752	0.048	0.517	0.483
1.0	1.0	0.950	0.950	0.050	0.511	0.489
0.8	1.2	0.752	1.152	0.048	0.509	0.491
0.5	1.5	0.462^5	1.462^5	0.037^5	0.505	0.495
0.2	1.8	0.182	1.782	0.018	0.502	0.498

*Values were calculated according to eq. 1.

It was found that the copolymer composition remains essentially equimolar in the range of studied feed compositions, and the product of this system is actually an alternating copolymer. Since known involvement of charge-transfer complexes in the formation of alternating copolymers the existence and participation of monomer complexes in the NVP-MCC copolymerization had been considered. We found that MCC, which has electron-withdrawing substituents is susceptible to donor-acceptor interactions with electron-rich monomer NVP. The monomer interactions were studied by PMR (FOSTER, 1969). The chemical shift measurements of the β-vinylic proton of MCC were used to evaluate the equilibrium constant of the complexation reaction between the monomers by application of Benesi-Hildebrand (BENESI *et al*,1949) method adapted for PMR data (HANNA, 1964). The constant K=0.05 ℓ/mole was found for the complexation reaction (1).

$$\text{MCC} + \text{NVP} \overset{K}{\rightleftarrows} \text{C} \qquad (1)$$

The terminal (MAYO *et al* 1944), the penultimate (MERZ *et al* 1946), and the complex (SEINER *et al* 1971) copolymerization models were applied for consistency with the results of the copolymer composition analysis. The terminal model equation was used in form ($r_2 = 0$):

$$y-1 = r_1 X \qquad (2)$$

where $y = m_1/m_2$ and $X = M_1/M_2$. The penultimate model was applied to the copolymerization of NVP and MCC with $r_2 = r'_2 = 0$ in the form of eq. 3.

$$y-1 = r'_1 X(1 + r_1 X)/(1+ r'_1 X) \qquad (3)$$

The complex model which considered in addition to the propagation by the uncomplexed monomers the participation of monomer donor-acceptor complexes, was used (eq.4).

$$y-1 = r_{1c}/r_{1c1} + r_{1c}[[M_1]/[C]-[M_2](y-1)/[C]r_{12}] \qquad (4)$$

In this equation $[M_1]$ and $[M_2]$ represent the concentration of free, uncomplexed NVP and MCC, respectively, and [C] is the concentration of the equimolar NVP-MCC monomer complex. The initial comonomer concentrations and these calculated on the basis of eq. 1 are presented in Table 1. Values for r_1 were selected until a straight line plot of (y-1) vs. $[M_1]/[C]-[M_2](y-1)/[C]r_1$ was produced. The "least squares" treatment of the data provided the slope $r_{1c} = 5.04 \cdot 10^{-3}$ and the intercept $r_{1c}/r_{1c1} = 9.55 \cdot 10^{-3}$ at $r_{12} = 0.08$. As shown in Fig. 1 the complex model fits the composition data much better than terminal and penultimate models of copolymerization.

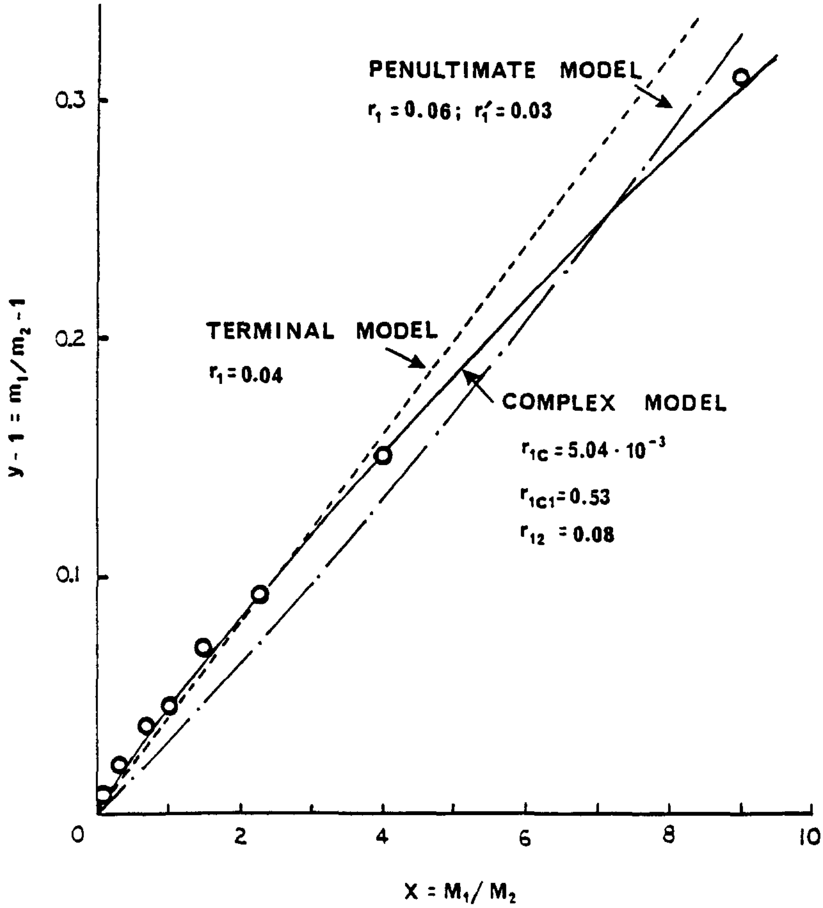

Figure 1. Analysis of the Copolymer Compositions Data in Terms of the Three Copolymerization Models.

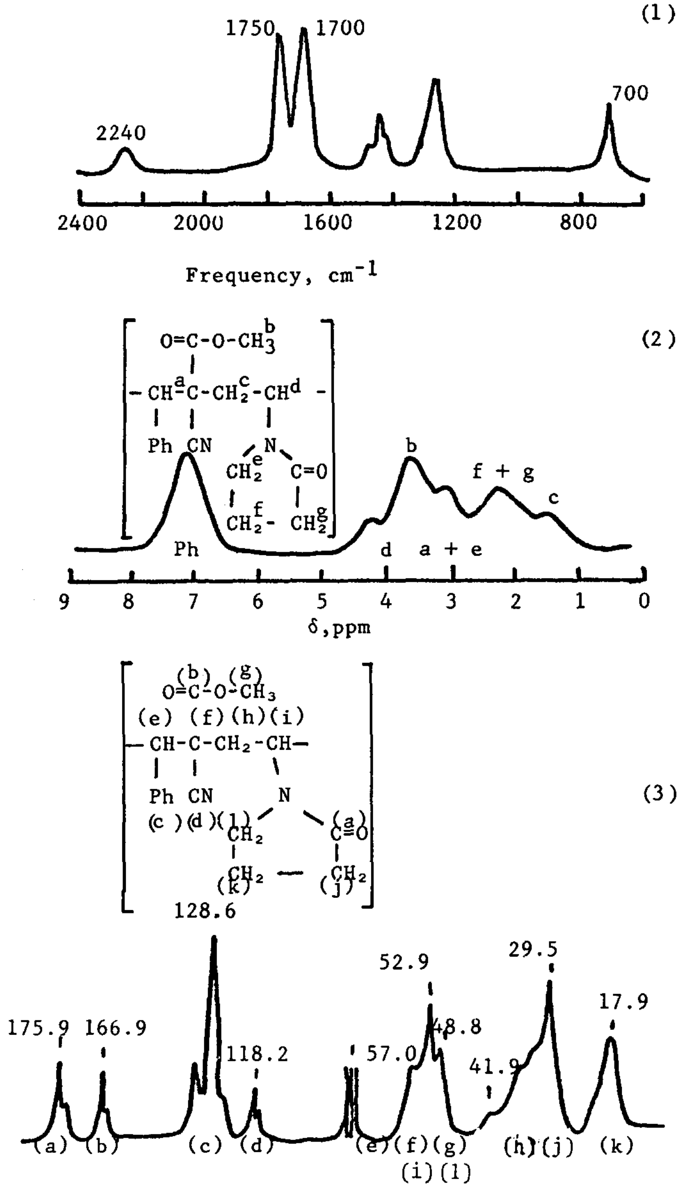

Figure 2. IR (1), PMR (2), and Carbon-13 NMR (3) spectra of equimolar MCC-NVP copolymer.

White powder-like MCC-NVP copolymers were soluble in chloroform, benzene, DMSO, DMF and insoluble in acetone, ethyl ether and hexane. IR spectrum of the equimolar MCC-NVP copolymer (Fig. 2) showed absorptions characteristic of both monomer units. Nitrile, carbonyl and phenyl groups of MCC monomer unit absorb at 2240, 1750 and 700 cm^{-1} respectively. An intense peak at 1700 cm^{-1} assigned to the carbonyl group vibrations of NVP on the basis of the same absorption in the spectrum of poly(N-vinyl pyrrolidone)(PNVP).

The 60 MHzPMR spectrum of the equimolar copolymer in $CDCl_3$ is given in Fig. 2 together with tentative assignment of peaks based on the spectrum of PNVP and copolymers of ethyl α-cyanocinnamate and benzilidenemalononitrile with vinyl acetate (KHARAS *et al* 1984).

The 25.16 MHz carbon-13 NMR spectrum of the copolymer solution was recorded in FT mode with proton decoupling and 2 seconds delay time. Tentative peak assignments given (Fig. 2) are based on the results of single frequency off-resonance proton decoupling experiments, expected chemical shift relationships, and comparison with the spectrum of PNVP (EBDON, 1983) and various copolymers of MCC.

REFERENCES

ALFREY, T. Jr. and GOLDFINGER, G., *J. Chem. Phys.* 12, 205(1944).
BENESI, H.A. and ASHBAUGH, A.L.: *J. Am. Chem. Soc.* 71,2703(1949).
BORROWS, E.T., HAWARD, R.N., PORGES, J. and STREET, J.: *J. Appl. Chem.*, 5, 379 (1955).
CARSON, B.B. and STOUGHTON, R.W.: *J. Am. Chem. Soc.*, 50, 2825(1928).
EBDON, J.R., HUCKERBY, T.N. and SENOGLES, E.: *Polymer*,24, 339(1983).
FOSTER, R.: Organic Charge-Transfer Complexes, Academic Press, London, 1969.
HALL, H.K. Jr. and YKMAN, P.: *Macromolecules*,10, 465(1977).
HALL, H.K. Jr. and DALY, R.C.: *Macromolecules*, 8, 22(1975).
HANNA, M.W. and ASHBAUGH, A.L.: *J. Phys. Chem.*,68, 811(1964).
HAYASHI, T.: *J. Org. Chem.*, 31, 3253(1966).
KHARAS, G. and KOHN, D.H.: *J. Polym. Sci., Polym. Chem.*, Ed. 21, 1457(1983).
KHARAS, G. and KOHN, D.H.: *J. Polym. Sci., Polym. Chem.*, Ed. 22, 577, 582(1984)
KREISEL, M., GARBATSKI, U. and KOHN, D.H.: *J. Polym. Sci.*, A2, 105(1964).
MERZ, E., ALFREY, T. Jr. and GOLDFINGER, G.: *J. Polym. Sci.*,1, 75(1946).
MAYO, F.R. and LEWIS, F.M.: *J. Am. Chem. Sci.*, 66, 1594(1944).
SEINER, J.A. and LITT, M.H.: *Macromolecules*, 4, 308(1971).

Accepted May 27, 1984