Copolymerization of N-Vinyl-2-pyrrolidone and 2-Phenyl-1,1-dicyanoethene

GREGORY B. KHARAS, *Polysar Incorporated, Plastics Division,*
P.O. Box 90, 29 Fuller Street, Leominster,
Massachusetts 01453, U.S.A.

Synopsis

Radical copolymerization of *N*-vinyl-2-pyrrolidone (NVP) with 2-phenyl-1,1-dicyanoethene (PDE) was studied in benzene at 70°C. Terminal, penultimate, and monomer complex participation kinetic models were applied to compositional data for best prediction of the copolymer composition. Both penultimate and complex models described satisfactorily the deviation from the terminal copolymerization model, although the complex model did not predict as well as the penultimate model at high NVP/PDE monomer feed ratios. Copolymerization reactivity ratios $r_{NVP} = 0.08$ and $r'_{NVP} = 1.8$ indicated substantial effect of the penultimate PDE monomer unit associated with polar repulsion of cyano groups. Equilibrium constant of NVP-PDE comonomer complex formation was found to be 0.08 L/mol as estimated by proton nuclear magnetic resonance (NMR) analysis of PDE's vinylic proton chemical shift upon complexation. Rate constants of propagation reactions were estimated by applying terminal complex copolymerization model.

INTRODUCTION

In recent years there has been interest in predominantly alternating copolymerization behavior in donor-acceptor monomer systems.[1-3] The involvement of charge-transfer interactions between comonomers and/or growing macroradicals in copolymerization was discussed in several publications.[4-6] In a continuation of our investigation of the monomer reactivities in copolymerization of electrophilic trisubstituted ethylenes, it was of interest to study copolymerization of 2-phenyl-1,1-dicyanoethene (PDE) and *N*-vinyl-2-pyrrolidone (NVP)*. Trisubstituted ethylene PDE does not polymerize with radical initiation, but copolymerizes easily with styrene[7] and vinyl acetate.[8] Two cyano substituents increase electrophilicity of the monomer double bonds and make it susceptible to donor-acceptor interactions with electron-rich monomers. The introduction of cyano groups on the α-atom of trisubstituted olefin promised stiffening of resulting polymer backbone with marked inhibition of rotation about the C—C bonds.

EXPERIMENTAL

Materials and Preparation of Comonomer

2-Phenyl-1,1-dicyanoethene (PDE) was prepared via a Knoevenagel condensation in 90% yield by method of Carson and Stoughton.[9] Benzalde-

---

*Systematic name 1-(2-oxo-1-pyrrolidinyl)ethylene.

Journal of Applied Polymer Science, Vol. 35, 733–741 (1988)
CCC 0021-8995/88/030733-09$04.00

hyde, malononitrile and piperidine (Aldrich) were used as received. The crude PDE was recrystallized twice from ethanol (mp 83–84°C).

ANAL. Calcd for $C_{10}H_6N_2$: C, 77.9; H, 3.90; N, 18.2. Found: C, 77.61; H, 3.95; N, 18.3; infrared (IR) (KBr), cm^{-1}, 2224, 1600, 1580, 1450, 1210, 970, 755, 680, 620, 520. ^1H (nuclear magnetic resonance)(NMR) (δ), ppm, 7.8 (vinyl, 1H), 7.3–8.1 (phenyl, 5H).

N-vinyl-2-pyrrolidone (NVP), (Aldrich) was dried over anhydrous $MgSO_4$ and vacuum distilled in the presence of hydroquinone (bp 68°C at 2 mmHg). Benzene was dried over $CaCl_2$ and distilled in nitrogen. Azobisisobutyronitrile (AIBN) (Aldrich) was twice recrystallized from ethyl alcohol and then dried under reduced pressure at room temperature.

Copolymerization

Copolymers of PDE and NVP were prepared in benzene solutions at 70°C using 0.0045 mol/L of AIBN as the initiator. After introduction of the monomers, AIBN and benzene, into pyrex tubes with a bulb at the lower end and a constriction near the upper end, the tubes were degassed and sealed. The total monomer concentration in each reaction was held constant at $2M$. After designated reaction time the copolymerization was stopped at low conversion by precipitation in a large excess of ethyl ether. The crude copolymers were filtered by suction using sintered glass crucible. The copolymers were washed repeatedly to ensure the complete removal of monomers and AIBN. Then copolymers were dried in a vacuum oven at 70°C for 100 h. Conversions were determined gravimetrically.

Copolymer Analysis

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 analyses.

Moisture analysis of the copolymers was done using Mitsubishi Moisture Meter, Model CA-05 with precision $\pm 3\ \mu g$ for 10 mg sample.

NMR Spectra

Proton NMR chemical shift measurements of NVP-PDE comonomer mixtures in $CDCl_3$ were conducted on a Varian EM-360L spectrometer at ambient temperature.

RESULTS AND DISCUSSION

Copolymerization Studies

The results of copolymerization of *N*-vinyl-2-pyrrolidone and 2-phenyl-1,1-dicyanoethene in benzene are given in Table I. The feed ratios of monomers and resultant copolymer compositions were used for studies of reactivity ratios. It has been shown that the chemical composition of a copolymer, both in the crude sense of overall composition and in the more detailed sense of the distribution of the units along the chain is controlled almost completely by

TABLE I
Copolymerization of *N*-Vinyl-2-pyrrolidone (M_1) and 2-Phenyl-1,1-dicyanoethene (M_2)

No.	M_1 in Feed (mol %)	Time (min)	Conversion (%)	Analysis (wt %) C	H	N	O[a]	Copolymer composition (mol %) m_1	m_2
B-280	90	10	3.5	69.45	5.93	15.30	9.32	71.78	28.22
B-290	80	12	9.1	70.07	5.92	15.31	8.68	67.73	32.27
B-300	70	10	8.2	70.40	5.94	15.29	8.37	65.79	34.21
B-310	60	8	5.2	70.56	5.90	15.31	8.23	64.87	35.13
B-311	50	6	3.6	70.75	5.68	15.64	7.93	62.97	37.03
B-312	40	10	3.2	71.02	5.75	15.59	7.64	61.05	38.95
B-313	30	10	1.8	71.04	6.05	15.57	7.34	59.05	40.95
B-314	20	15	1.2	71.50	5.84	15.60	7.06	57.15	42.85
B-315	10	20	0.8	71.63	5.85	15.78	6.74	54.95	45.05

[a] Calculated.

the nature of the propagation steps. Considering four propagation steps (1) and assuming the reactivity of the propagation chain in a copolymerization to be dependent on the terminal monomer unit at the groving end, Alfrey and Goldfinger[10] and Lewis and Mayo[11] derived the following equation regarding the overall copolymer composition with the composition of the monomer mixture:

$$\begin{aligned} \sim M_1^{\cdot} + M_1 &\xrightarrow{k_{11}} \sim m_1 m_1^{\cdot} \\ \sim M_1^{\cdot} + M_2 &\xrightarrow{k_{12}} \sim m_1 m_2^{\cdot} \\ \sim M_2^{\cdot} + M_1 &\xrightarrow{k_{21}} \sim m_2 m_1^{\cdot} \\ \sim M_2^{\cdot} + M_2 &\xrightarrow{k_{22}} \sim m_2 m_2^{\cdot} \end{aligned} \tag{1}$$

$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \tag{2}$$

where m_1 and m_2 represent the molar concentrations of the two monomers in the copolymer, $[M_1]$ and $[M_2]$ the molar concentrations in the monomer mixture, r_1 and r_2 reactivity ratios of propagation rate constants k_{11}/k_{12} and k_{22}/k_{21}, respectively. Application of the terminal copolymerization model[10,11] was done by treatment of the compositional data in Table I according to the method of Kelen and Tudos,[12] which applies Eq. (3) for graphical determination of the copolymerization parameters:

$$G/\alpha + F = (r_1 + r_2/\alpha)F/\alpha + F - r_2/\alpha \tag{3}$$

where $G = X(1 - 1/Y)$, $X = [M_1]/[M_2]$ in monomer feed, $F = X^2/Y$ and $Y = m_1/m_2$ in the copolymer; the parameter α is equal to $(F_M F_m)^{0.5}$, F_M and F_m being the highest and the lowest values of F.

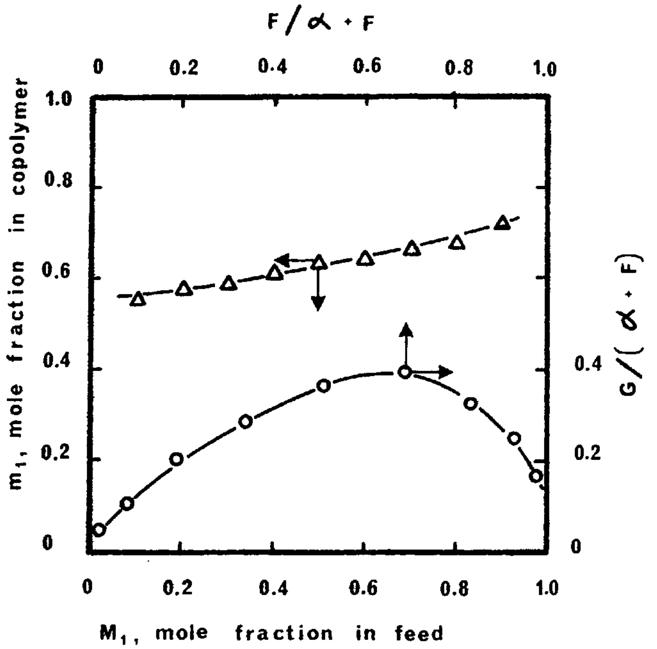

Fig. 1. Copolymer composition diagram and Kelen-Tudos plot for NVP (M_1)-PDE (M_2) copolymerization.

Nonlinearity of the plot (Fig. 1) demonstrates poor applicability of the terminal model to NVP-PDE copolymerization system.

Deviations of polymer composition from that predicted by the terminal model have been ascribed to penultimate effects[13] or monomer complex participation.[14] In the copolymerization of NVP (M_1) with PDE (M_2), PDE is incapable of self propagation, thus the consideration of penultimate effect involves the following propagation equations (4):

$$\begin{aligned} &\sim m_1 m_1^{\cdot} + M_1 \xrightarrow{k_{111}} \sim m_1 m_1 m_1^{\cdot} \\ &\sim m_1 m_1^{\cdot} + M_2 \xrightarrow{k_{112}} \sim m_1 m_1 m_2^{\cdot} \\ &\sim m_2 m_1^{\cdot} + M_1 \xrightarrow{k_{211}} \sim m_2 m_1 m_1^{\cdot} \\ &\sim m_2 m_1^{\cdot} + M_2 \xrightarrow{k_{212}} \sim m_2 m_1 m_2^{\cdot} \end{aligned} \tag{4}$$

with reactivity ratios $r_1 = k_{111}/k_{112}$ and $r_1' = k_{211}/k_{212}$.

Copolymerization parameters $r_1 = 0.08$ and $r_1' = 1.8$ were estimated by trial and error using Eq. (5).[15]

$$r_1 = \left[(Y - 1)/X^2\right](1/r_1') + (Y - 2)X \tag{5}$$

where $Y = m_1/m_2$ and $X = M_1/M_2$. For each pair of X and Y, r_1 was plotted as a linear function of $1/r_1'$ and the best intersection of the various lines was

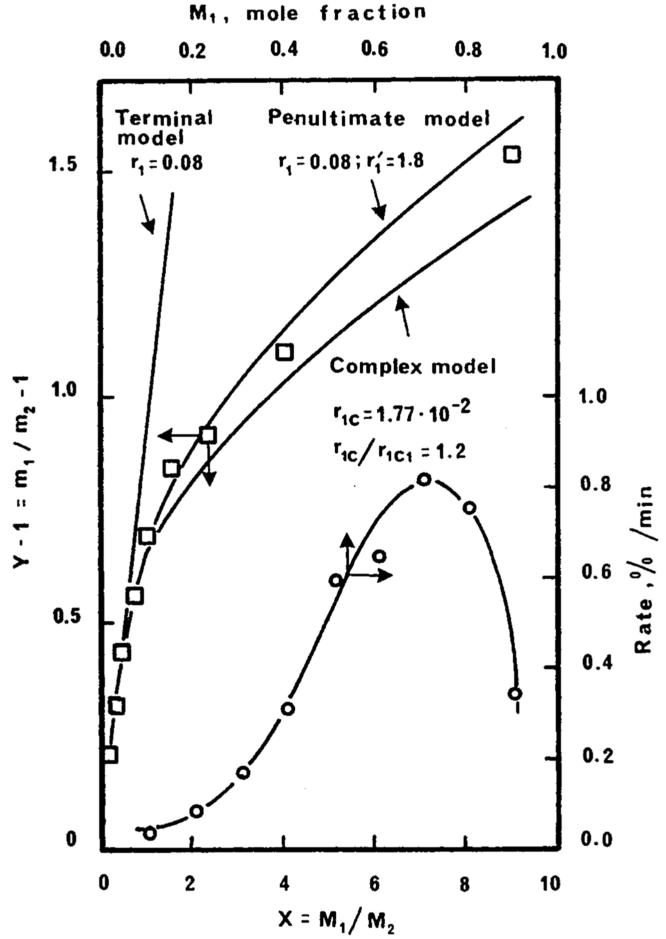

Fig. 2. Rate of conversion and examination of the NVP-PDE composition data in terms of the three copolymerization models.

determined. The solid curve in Figure 2 was plotted by inserting the values of $r_1 = 0.08$ and $r_1' = 1.8$ into Merz's equation (6).[13]

$$Y - 1 = r_1'X(1 + r_1X)/(1 + r_1'X) \tag{6}$$

Thus the application of the penultimate model greatly improves the agreement between predicted and experimental values. The effect of the penultimate PDE unit, similar to one found in copolymerization of 1,2-substituted ethylenes,[13] associated with polar repulsion of cyano groups where nitrogen atom of dipolar group is exposed and accessible, whereas the carbon atom is linked to further structure and therefore is more shielded. Consequently, interactions between terminal atoms, which are of like polarity, are configurationally much more likely than those between opposite charges, and net effect is one of repulsion.

2-Phenyl-1,1-dicyanoethene has two electron-withdrawing cyano substituents which makes its electron-deficient double bond susceptible to the formation of charge transfer complexes with electronegative monomers. A mechanism involving the participation of both the free monomers and monomer complexes in propagation reactions was considered by Seiner and Litt[16] and Tsuchida and Tomono.[17] Terminal complex model[16] in addition to Eq. (1) include four propagation equations (7):

$$\begin{aligned}
&\sim m_1^{\cdot} + (M_1M_2) \xrightarrow{k_{1c1}} \sim m_1m_1m_2^{\cdot} \\
&\sim m_1^{\cdot} + (M_2M_1) \xrightarrow{k_{1c2}} \sim m_1m_2m_1^{\cdot} \\
&\sim m_2^{\cdot} + (M_1M_2) \xrightarrow{k_{2c1}} \sim m_2m_1m_2^{\cdot} \\
&\sim m_2^{\cdot} + (M_2M_1) \xrightarrow{k_{2c2}} \sim m_2m_2m_1^{\cdot}
\end{aligned} \tag{7}$$

The terminal complex equation (8)[16] can be used for analysis of NVP-PDE copolymerization data, assuming $k_{22} = k_{2c2} = 0$.

$$Y - 1 = r_{1c}/r_{1c1} + r_{1c}([M_1]/[C] - [M_2](Y-1)/[C]r_{12}) \tag{8}$$

where $[M_1]$ and $[M_2]$ represent the concentrations of free, uncomplexed NVP and PDE, respectively; $Y = m_1/m_2$; $[C]$ is concentration of equimolar NVP–PDE complex; $r_{12} = k_{11}/k_{12}$; $r_{1c} = k_{11}/(k_{1c1} + k_{1c2})$; and $r_{1c1} = k_{11}/k_{1c1}$. Application of Eq. (8) requires a knowledge of the concentrations of uncomplexed monomers in each of the monomer feeds. These were calculated from the initial concentrations of monomers in the feeds using the value of the equilibrium constant for the NVP–PDE monomer complex formation, $K = 0.08$ L/mol, which was determined by proton NMR. The chemical shift measurements of the vinylic proton of PDE were utilized to evaluate K by application of Benesi-Hildebrand method[18] adapted for NMR data.[19] Table II presents compositional data assuming relatively weak monomer complex formation NVP + PDE $\rightleftharpoons$ C. Values for r_{12} were selected until a straight-line

TABLE II
Compositional Data of NVP (M_1)-PDE (M_2) Copolymerization

Feed composition, mol/L					Copolymer composition	
Loaded		Calculated[a]				
$[M_1^0]$	$[M_2^0]$	$[M_1]$	$[M_2]$	$[C]$	m_1 mol fr.	$m_1/m_2 - 1$
1.8	0.2	1.77	0.17	0.03	0.72	1.54
1.6	0.4	1.55	0.35	0.05	0.68	1.10
1.4	0.6	1.33	0.53	0.07	0.66	0.92
1.2	0.8	1.12	0.72	0.08	0.65	0.85
1.0	1.0	0.92	0.92	0.08	0.63	0.70
0.8	1.2	0.72	1.12	0.08	0.61	0.57
0.6	1.4	0.53	1.33	0.07	0.59	0.44
0.4	1.6	0.35	1.55	0.05	0.57	0.33
0.2	1.8	0.17	1.77	0.03	0.55	0.22

[a] Calculated based on $[C] = K[M_1][M_2]$.

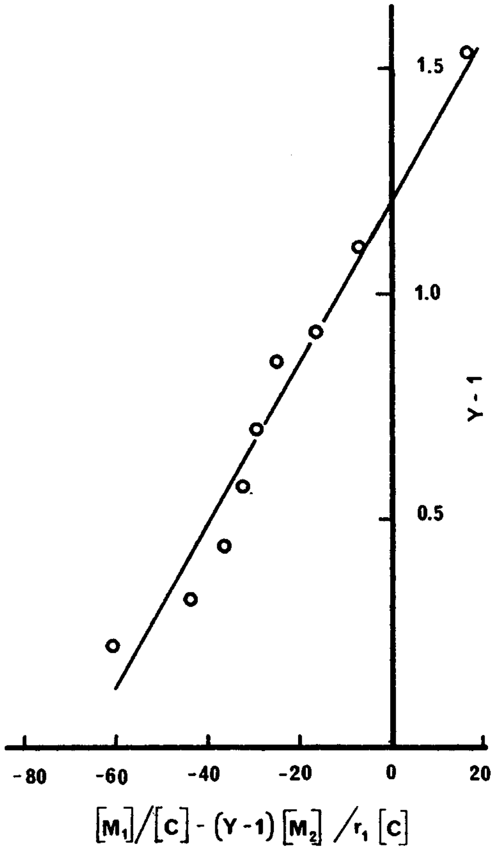

Fig. 3. Determination of the reactivity ratios r_{1c1} and r_{1c} according to Eq. (8).

plot of $(Y - 1)$ versus $([\mathrm{NVP}]/[\mathrm{C}] - [\mathrm{PDE}](Y - 1)/[\mathrm{C}]r_{12})$ was produced (Fig. 3). The least-squares treatment of the data provides the slope $r_{1c} = 1.77 \times 10^{-2}$ and the intercept $r_{1c}/r_{1c1} = 1.2$.

Comparison of the data in Figure 2 shows that the terminal complex model can predict the NVP-PDE copolymer composition although not as well as the multimate model especially at high monomer feed ratios.

The application of the complex model to the composition data allows estimation of some copolymerization parameters, taking into account the literature value of the NVP propagation constant, $k_p = 950$ L/mol.[20] Thus, because $k_{11} = 950$ L/mol s and $r_{12} = k_{11}/k_{12} = 0.2$, $k_{12} = 4800$ L/mol s. Reactivity ratio $r_{1c1} = 0.15$ can be obtained easily combining r_{1c} and r_{1c}/r_{1c1}. Propagation constant $k_{1c1} = 6400$ is calculated knowing that $k_{1c1} = k_{11}/r_{1c1}$. The rate constant for addition to the PDE side of the complex $k_{1c2} = K_{1c} - K_{1c1} = 4700$ L/mol s as well as the reactivity ratio $r_{1c2} = k_{11}/k_{1c2} = 0.02$ can be obtained from $k_{1c} = k_{11}/r_{1c} = 5300$ L/mol s.

Analysis of the copolymerization parameters (Table III) show that the fastest reaction is the addition of the monomer complex by the PDE side to a chain with NVP terminal unit [Eq. (7)]. The addition of the monomer complex happens more than 55 times faster than homopropagation of NVP.

TABLE III
Kinetic Parameters Determined by the Application of Complex Model for the NVP-PDE Copolymerization

Rate constants, L/mol sec					Reactivity ratios			
k_{11}	k_{12}	k_{1c}	k_{1c1}	k_{1c2}	r_{12}	r_{1c}	r_{1c1}	r_{1c2}
950	4800	5300	6400	4700	0.2	0.02	0.15	0.02

The attack of the NVP-terminated macrochain by NVP side of the NVP-PDE complex is 7 times less probable than by the PDE side of it, because at the ground state, the complex of this small equilibrium constant is thought to be almost exclusively made of the no-bond state in which the components of the complex still retain their original polarity.[21] The increase of NVP content in the copolymer with the increase of NVP feed ratio may be associated with the decrease of complex concentration, which has maximum at equimolar feed composition. The fact that the rate of the NVP-PDE copolymerization is not maximized at equimolar ratio of comonomers in the feed (Fig. 2) also indicates the participation of free monomers[22] in the propagation reactions.

CONCLUSIONS

Copolymerization of *N*-vinyl-2-pyrrolidone and 2-phenyl-1,1-dicyanoethene results in alternating copolymers with isolated PDE units and sequences of NVP monomer units. The copolymer compositional data was analyzed in terms of terminal, penultimate, and terminal complex kinetic models of copolymerization. The best fit of the experimental values was observed in the case of penultimate model. The terminal complex model involving charge transfer NVP-PDE monomer complexes as well as addition of free monomers in propagation reactions could predict reasonably well copolymer compositions at less than equimolar feed ratios but resulted in deviations at higher NVP feed content. The complex model fit might be improved if penultimate effects were taken into consideration.

The author is grateful to Polysar Incorporated, Plastics Division for support of this research.

References

1. K. Fujimori and I. E. Graven, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 559 (1986).
2. S. Iwatsuki, T. Itoh, M. Shimizu, and S. Ishikawa, *Macromolecules*, **16**, 1407 (1983).
3. D. J. T. Hill, J. H. O'Donnell, and P. W. O'Sullivan, *Macromolecules*, **18**, 9 (1985).
4. P. Karad and S. Schneider, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 1137 (1978).
5. G. S. Georgiev, V. B. Golubev, and V. P. Zubov, *Vysokomol, Suedin.*, **A20**, 1608 (1978).
6. K. G. Olson and G. B. Butler, *Macromolecules*, **16**, 707, (1983).
7. M. Kreisel, V. Garbatsky, and D. H. Kohn, *J. Polym. Sci.*, **A2**, 105 (1964).
8. G. Kharas and D. H. Kohn, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 583 (1984).
9. B. B. Carson and R. W. Stoughton, *J. Am. Chem. Soc.*, **50**, 2825 (1928).
10. T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944).
11. F. Lewis and F. Mayo, *J. Am. Chem. Soc.*, **60**, 1594 (1944).
12. T. Kelen and F. Tudos, *J. Macromol. Sci., Chem.*, **A9**, 1 (1975).
13. E. Merz, T. Alfrey, and G. Goldfinger, *J. Polym. Sci.*, **1**, 75 (1946).
14. W. G, Barb, *J. Polym. Sci.*, **10**, 49 (1953).
15. W. G. Barb, *J. Polym. Sci.*, **11**, 117 (1953).

16. J. A. Seiner and M. Litt, *Macromolecules*, **4**, 308 (1971).
17. E. Tsuchida and T. Tomono, *Makromol. Chem.*, **141**, 265 (1971).
18. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
19. M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964).
20. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, II, 51, 2nd ed., J. Wiley & Sons, Inc., New York, 1975.
21. H. B. Friedrich and W. B. Person, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
22. M. Yoshimura, T. Nogami, M. Yokoyama, H. Mikawa, and Y. Shirota, *Macromolecules*, **9**, 211 (1976).

Received January 26, 1987
Accepted May 25, 1987