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Mechanism of Radical Copolymerizations of *N*-Vinylcarbazole with Diethyl and Dimethyl Maleate

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ABSTRACT: Free-radical initiated copolymerizations of *N*-vinylcarbazole (VCZ) (M_1) with diethyl maleate (M_2) or dimethyl maleate (M_2') have been studied in connection with the 1:1 alternating radical copolymerization of VCZ with the isomeric diethyl fumarate. The compositions of the copolymers vary from 1:1 alternation to increasingly VCZ rich with the increase of VCZ in the monomer feed (Table I). Results are strongly in favor of the mechanism involving the participation of free monomers in the alternating copolymerization (eq 2–5). Copolymer composition is well reproduced with $r_1 = 0.27$ (M_2), 0.26 (M_2'); $r_2 = 0$. This mechanism leads to the copolymerization rate eq 14, which fits well the experimental data (Figure 2).

The mechanism for the alternating radical copolymerization has recently attracted a great deal of attention, and is still controversial. Some propose the charge-transfer model to explain the alternation, that is, the charge-transfer complex formed between monomer pairs (the charge-transfer complexed monomer) homopolymerizes to yield the 1:1 alternating copolymer.[1] Others insist that the cross-propagation of free monomers, the transition state of which is stabilized, is operative.[2]

We have been investigating free-radical initiated copolymerizations of *N*-vinylcarbazole (VCZ), a typical electron-donating monomer which has recently received great attention in the field of the so called charge-transfer polymerization, with a series of electron-accepting monomers with a hope of elucidating the mechanism of the alternating radical copolymerization.

In the previous paper,[3] we reported the first known examples of the 1:1 alternating radical copolymerization of VCZ with diethyl fumarate or fumaronitrile, and proposed a new model for the alternating radical copolymerization. The generalized mechanism which we have proposed involves the participation of both free monomers and the charge-transfer complexed monomer (CT-complexed monomer) in the propagation step of the polymerization with a varying degree of their contributions to the polymerization which depends on the reaction system. Our model stands on the basis that the alternation can be brought about by the stabilization of the transition state of the cross-reaction of both free monomers and the CT-complexed monomer, and that the participation of the CT-complexed monomer in the polymerization makes contribution to the enhancement of the polymerization rate due to its higher reactivity than the free monomer.

Our continued interest in this field has led us to extend the study to the copolymerization of VCZ with the isomeric electron-accepting monomer of diethyl fumarate and diethyl and dimethyl maleate. The present results are consistent with our model and seem to provide the experimental evidence for the participation of the free monomer in the alternating radical copolymerization.

Experimental Section

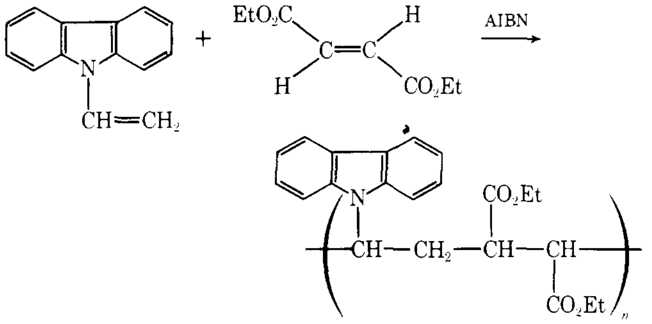
Materials. *N*-Vinylcarbazole (VCZ) and 2,2′-azobisisobutyronitrile (AIBN) were purified and dried as described in the previous paper.[4] Diethyl maleate and dimethyl maleate which were obtained commercially (WAKO Pure Chemical Ind. Ltd.) as pure grade reagents were dried over calcium chloride, and distilled twice from calcium hydride in vacuo under a nitrogen stream, bp 71.5°C (2 mm) and 60.5°C (2 mm), respectively. The purity of the material was checked by means of GLC.

Polymerization Procedure. All copolymerizations were carried out in a benzene solution using AIBN as an initiator. The total monomer concentration was fixed as 1.0 *M*, the monomer feed ratio being varied widely. The initiator concentration was 1.0×10^{-3} *M*. The polymerization solution contained in a glass tube, ca. 1.5 cm in diameter, was evacuated at 2×10^{-2} Torr by means of several freeze–pump–thaw cycles, sealed off and then allowed to stand for an appropriate time in a thermostat maintained at 80 ± 0.1°C. The polymerization was stopped at low conversions. The polymerization solution was chilled and poured into a large volume of MeOH to precipitate the polymer. The polymers were collected by filtration with a glass filter, washed with MeOH repeatedly, dried in vacuo, and weighed. The polymers were reprecipitated twice from benzene with MeOH and submitted to analyses.

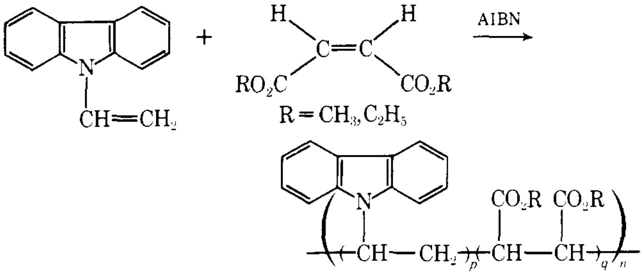
Apparatus. Ir spectra were taken with the Hitachi EPI-G2 and Jasco Ir-G infrared spectrophotometers. Uv spectra were taken with a Hitachi 124 spectrophotometer. Molecular weights of polymers were determined with a Mechrolab VPO Model 302 in benzene at 25°C.

Results and Discussion

N-Vinylcarbazole (VCZ) was copolymerized with diethyl and dimethyl maleate (DEM, DMM) in a benzene solution under initiation with AIBN to produce copolymers the composition of which varied with the monomer feed composition from 1:1 to VCZ rich as described later, while the copolymerization of VCZ with the trans-isomeric diethyl fumarate always yielded 1:1 alternating copolymers regardless of the monomer feed composition.[3]



1:1 alternating copolymer



$p = 1, 2, \ldots; q = 1$

Characterization of Copolymers. Both VCZ-DEM and VCZ-DMM copolymers were obtained as white powders. The copolymer formation was confirmed from the solubility behaviors, elementary analyses, ir and uv spectra of the copolymer, and determination of the number-average molecular weight. The VCZ-DEM and VCZ-DMM copolymers with varying copolymer compositions softened in the range ca. 167-265°C and 202-286°C, respectively. The solubility behaviors of both copolymers, which varied slightly with the copolymer composition, were generally similar to those of VCZ homopolymer, but copolymers were fairly soluble even in carbon tetrachloride in which homopolymer is not soluble. The ir spectra of VCZ-DEM and VCZ-DMM copolymers showed a strong carbonyl absorption at 1720 and 1730 cm^{-1}, respectively. The characteristic ir absorption peaks at 963 and 866 cm^{-1} due to the vinyl group on a nitrogen atom observed in the VCZ monomer disappeared in both copolymers. The composition of the copolymers determined from the nitrogen analysis shows that it is almost 1:1 for the monomer feed compositions where the VCZ molar ratio is less than ca. 0.5, then deviating from 1:1 to increasingly VCZ rich as the molar ratio of VCZ in the monomer feed is increased. The copolymers of the 1:1 composition are regarded as the alternating copolymers since both DEM and DMM monomers do not homopolymerize under the present reaction conditions. The compositions and molecular weights of the copolymers are summarized in Table I. The uv absorption spectra of the copolymers reflect the composition of the copolymers. We have reported that the positions of the low-energy π–π^* absorption maxima due to the carbazole chromophore shift toward the blue region by about 10 to 5 nm for the 1:1 alternating copolymer of VCZ with the electron-accepting monomer as compared with those for the VCZ homopolymer, and that extent of the blue shift appears to be dependent on the electron-accepting strength of the comonomer in the monomer state.[3] As can be seen in Table II, the positions of the low-energy π–π^* maxima due to the carbazole chromophore in the copolymers are approximately 6 to 5 nm blue shifted for the copolymers with almost 1:1 composition with respect to those for the VCZ homopolymer (λ_{max} = 330, 344 nm), gradually approaching the values for the VCZ homopolymer as the composition of the copolymer becomes VCZ rich. The copolymer composition is also reflected in the emission spectra. That is, no excimer fluorescence is observed in the copolymers with almost 1:1 composition, but the VCZ-rich copolymer shows the excimer fluorescence because of the presence of two adjacent carbazole chromophores. The details of the emission spectra of the VCZ copolymers were discussed before.[4]

Table I
Compositions and Molecular Weights of the Copolymers

Mol fraction of VCZ in monomer feed	Nitrogen content in copolymer, %		Mol fraction of VCZ in copolymer		Softening point, °C	Mol wt
VCZ–DEM Copolymer						
0.9	5.45		0.73		280	11000
0.8	5.34		0.71		220	13000
0.7	4.60		0.61		215	15700
0.6	4.64		0.61		210	11900
0.5	4.22		0.55		203	12200
0.4	3.97		0.52		197	11600
0.3	4.03		0.53		193	
0.2	4.05		0.53		187	9500
0.1	3.59		0.47		180	
VCZ–DMM Copolymer						
	(I)	(II)	(I)	(II)		
0.9	5.87	5.87	0.76	0.76	286	12000
0.8	5.38	5.31	0.68	0.67	237	8000
0.7	5.02	5.39	0.63	0.68	212	5200
0.6	4.84	5.18	0.60	0.65	208	5300
0.5	4.83	4.83	0.60	0.60	207	5700
0.4	4.80	4.73	0.59	0.58	208	5000
0.3	4.55	4.43	0.56	0.54	203	5300
0.2		4.29		0.52	202	
0.1	4.18		0.50			

Table II
Low-Energy π–π^* Absorption Maxima of the Copolymers[a]

Mol fraction of VCZ in copolymer	Max$_1$, nm	Max$_2$, nm
VCZ–DEM Copolymer		
0.80	328.5	341.5
0.71	327.0	339.0
0.60	326.0	338.5
0.51	325.0	338.0
VCZ–DMM Copolymer		
0.76	328.5	340.0
0.68	326.5	338.5
0.65	326.0	338.0
0.59	325.5	338.0
0.58	325.0	338.0
0.55	325.0	338.0
0.52	325.0	337.5
0.50	324.5	337.5

[a] In H_4 furan solution.

Table III
Initial Copolymerization Rate (R_p) in the VCZ–DEM System[a]

Mol fraction of VCZ in monomer feed	Monomer feed, mg		Polym time, min	Polymer yield, mg	R_p[d] × 10^3, mol/l./min
	VCZ	DEM			
1.0[b]	482.5	0	30	231.8	16.01
0.9	868.5	86.0	15	82.7	5.89
0.8	772.0	172.0	30	107.8	3.85
0.7	675.5	258.0	30	69.9	2.52
0.6	579.0	344.0	30	56.0	2.02
0.5	482.5	430.0	30	43.4	1.58
0.4	386.0	516.0	30	32.8	1.20
0.3	289.5	602.0	30	21.8	0.79
0.2[c]	193.0 × 3	688.0 × 3	30	39.1	0.47
0.1[c]	96.5 × 3	774.0 × 3	30	11.5	0.14

[a] Reaction conditions: [VCZ] + [DEM] = 1.0 *M*, [AIBN] = 1 × 10^{-3} *M*; solvent, benzene (5 ml); temp, 80°C. [b] Solvent, benzene (2.5 ml). [c] Solvent, benzene (15 ml). [d] $R_p = -d([M_1] + [M_2])/dt$ mol/l./min: M_1 = VCZ, M_2 = DEM.

Table IV
Initial Copolymerization Rate (R_p) in the VCZ–DMM System[a]

Mol fraction of VCZ in monomer feed	Monomer feed, mg		Polym time, min	Polymer yield, mg	R_p[b] × 10^3, mol/l./min
	VCZ	DMM			
0.9	868.5	72.0	10	100.1	11.05
0.8	772.0	144.0	10	62.1	7.00
0.7	675.5	216.0	10	52.3	5.98
0.6	579.0	288.0	10	40.0	4.62
0.5	482.5	360.0	10	32.2	3.72
0.4	386.0	432.0	10	24.0	2.77
0.3	289.5	504.0	10	16.2	1.90
0.2	193.0	576.0	10	8.0	0.94
0.1	96.5	648.0	60	19.1	0.35

[a] Reaction conditions: [VCZ] + [DMM] = 1.0 *M*, [AIBN] = 1 × 10^{-3} *M*; solvent, benzene (5 ml); temp, 80°C. [b] $R_p = -d([M_1] + [M_2])/dt$ mol/l./min: M_1 = VCZ, M_2 = DMM.

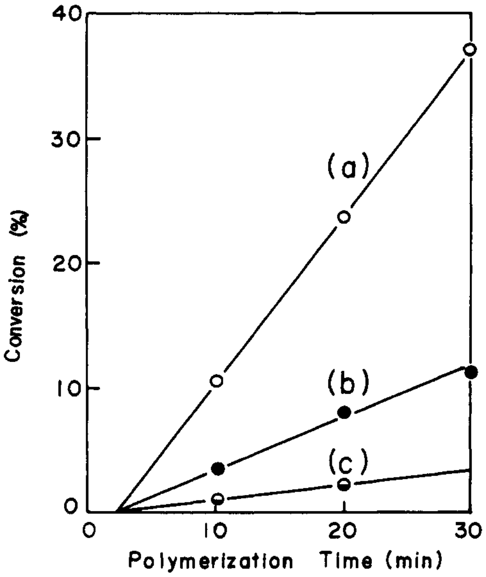


Figure 1. Conversion (polymer weight/weight of total monomers) vs. polymerization time in the VCZ–DMM system; [AIBN] = 1 × 10^{-3} *M*; temp, 80°C; solvent, benzene: (a) [VCZ] = 0.8 *M*, [DMM] = 0.2 *M*; (b) [VCZ] = 0.5 *M*, [DMM] = 0.5 *M*; (c) [VCZ] = 0.2 *M*, [DMM] = 0.8 *M*.

Copolymerization Rate and Chain Transfer. The conversions (polymer weight/weight of total monomers) were plotted as functions of polymerization time in Figure 1, which shows a linear relationship under 40% conversion for different monomer feed ratios. In Figure 2 are shown the plots of the initial rates of copolymerization ($R_p = -d([M_1] + [M_2])/dt$ mol/l./min) against the monomer feed ratio. It is evident that the copolymerization rate increases with the VCZ molar ratio in the monomer feed and the increase in the rate becomes striking when the VCZ molar ratio in the monomer feed exceeds ca. 0.5. The results are also summarized in Tables III and IV.

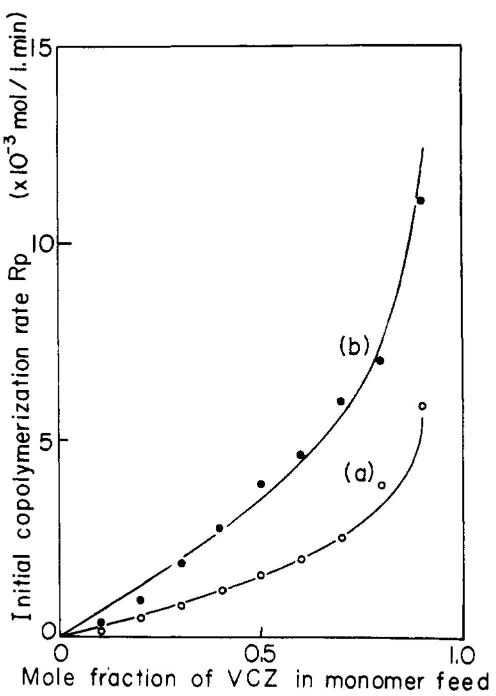


Figure 2. Initial copolymerization rates ($-d([M_1] + [M_2])/dt$) vs. monomer feed molar ratio in the VCZ–DEM and VCZ–DMM systems; M_1 = VCZ, M_2 = DEM or DMM; [VCZ] + [DEM or DMM] = 1.0 *M*; [AIBN] = 1 × 10^{-3} *M*; temp, 80°C; solvent, benzene; (○, ●) experimental data; (—) theoretical curves, least-squares plot of eq 21: (a) VCZ–DEM system; (b) VCZ–DMM system.

The copolymerization rate (R_p) is in proportion to 0.4 order of the initiator concentration, as shown in Figure 3, which suggests that the bimolecular termination occurs predominantly.

Relatively low molecular weights of the copolymers obtained suggest that the chain-transfer reaction is operative in these copolymerizations, which is indicated from the plot $1/Pn$ vs. R_p ($1/Pn = AR_p + C_M$), as shown in Figure 4; the value of C_M (chain-transfer constant to the monomer) is 0.75 × 10^{-2} in the VCZ–DEM system.

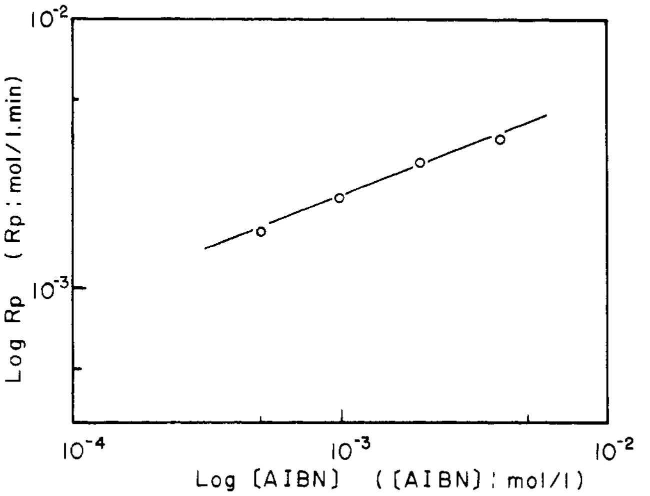


Figure 3. Initial copolymerization rates ($-\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])/\mathrm{d}t$) vs. initiator concentration in the VCZ-DEM system; M_1 = VCZ, M_2 = DEM; [VCZ] = [DEM] = 0.5 *M;* temp, 80°C; time, 10 min; solvent, benzene.

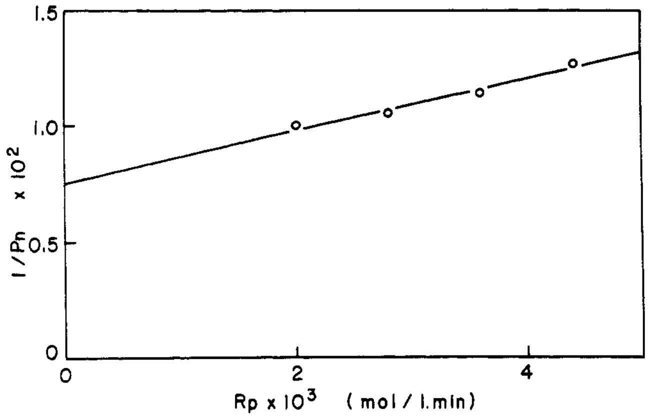


Figure 4. Plot of $1/Pn$ vs. R_p for the varied initiator concentrations in the VCZ-DEM system; [VCZ] = [DEM] = 0.5 *M;* temp, 80°C; time, 10 min; solvent, benzene.

Mechanism of the Copolymerization. Based upon our model for the alternating radical copolymerization,[3] it is thought that the propagation process of the present copolymerization systems possibly involves the following reactions

$$\mathrm{m}_1\cdot + \mathrm{M}_1 \xrightarrow{K_{11}} \mathrm{m}_1\cdot \tag{1}$$

$$\mathrm{m}_1\cdot + \mathrm{M}_2 \xrightarrow{k_{12}} \mathrm{m}_2\cdot \tag{2}$$

$$\mathrm{m}_2\cdot + \mathrm{M}_1 \xrightarrow{k_{21}} \mathrm{m}_1\cdot \tag{3}$$

$$\mathrm{m}_1\cdot + \mathrm{M}_2\mathrm{M}_1 \xrightarrow{k_{1c}} \mathrm{m}_1\cdot \tag{4}$$

$$\mathrm{m}_2\cdot + \mathrm{M}_1\mathrm{M}_2 \xrightarrow{k_{2c}} \mathrm{m}_2\cdot \tag{5}$$

where M_1, M_2, $\mathrm{M}_1\mathrm{M}_2$, ($\mathrm{M}_2\mathrm{M}_1$) stand for VCZ, DEM, DMM, and CT-complexed monomer, respectively. The symbols $\mathrm{m}_1\cdot$ and $\mathrm{m}_2\cdot$ represent the corresponding growing chain radicals, and k_{11}, k_{12}, k_{21}, k_{1c}, and k_{2c} are the rate constants in each reaction.

In the present copolymerization systems, no charge-transfer complex formation between monomer pairs is detected spectroscopically. We have suggested on the basis of

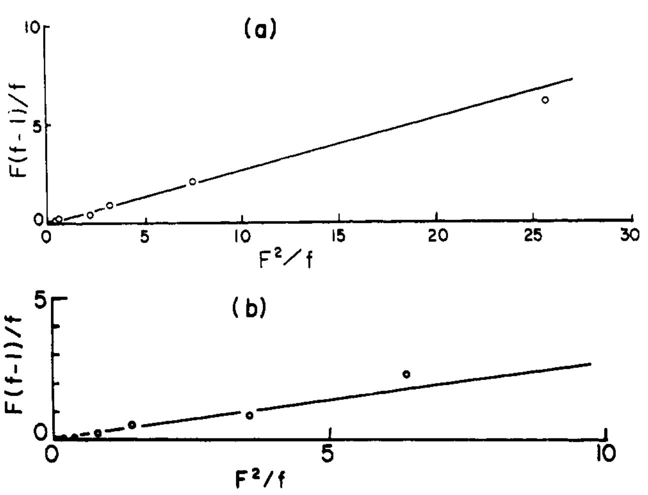


Figure 5. Fineman–Ross plot; $\mathrm{d}[\mathrm{M}_1]/\mathrm{d}[\mathrm{M}_2] = ([\mathrm{M}_1]/[\mathrm{M}_2])\,[(r_1[\mathrm{M}_1] + [\mathrm{M}_2])/[\mathrm{M}_1]]$; M_1 = VCZ, M_2 = DEM or DMM; $F = [\mathrm{M}_1]/[\mathrm{M}_2]$, $f = \mathrm{d}[\mathrm{M}_1]/\mathrm{d}[\mathrm{M}_2]$: (a) VCZ–DEM system, (b) VCZ–DMM system.

the rate features that the contribution of the charge-transfer complex to the polymerization is negligibly small even in the VCZ–diethyl fumarate alternating copolymerization system where the charge-transfer complex formation is detected spectroscopically. Therefore, in the present copolymerization systems, the reactions 1, 2, and 3 are considered to be the major ones which are operative in the propagation process.

Assuming the participation of only free monomers in the present systems, monomer reactivity ratios were calculated from the Fineman–Ross plot (Figure 5). Values thus obtained were $r_1 = 0.27$ and $r_2 = 0$ for the VCZ–DEM system, and $r_1 = 0.26$ and $r_2 = 0$ for the VCZ–DMM system, showing that the rate constant k_{12} is only ca. 4 times larger than k_{11} in these copolymerization systems. Thus, the reaction 1 can compete with the reaction 2 as the monomer feed composition becomes sufficiently rich in VCZ, resulting in the deviation from the 1:1 alternating to VCZ rich in the copolymer composition in these systems. It is of interest to note that the VCZ–diethyl fumarate system always yields the 1:1 alternating copolymer regardless of the monomer feed composition. The striking difference in the copolymerization behavior between diethyl fumarate and DEM may be ascribed to much less reactivity of the cis isomer than the trans isomer in the monomer state, as reflected in their Q values[5] (Q = 0.059, 0.09, and 0.61 for DEM, DMM, and diethyl fumarate, respectively).

Now, let us explain qualitatively the copolymerization rate features shown in Figure 2. As discussed above, in VCZ–DEM and VCZ–DMM systems, the reactions 1, 2, and 3 are the major propagation processes, reactions 4 and 5 being negligible. If a bimolecular termination is assumed to occur, three termination modes are possible.

$$\mathrm{m}_1\cdot + \mathrm{m}_1\cdot \xrightarrow{k_{\mathrm{t}11}} \text{polymer} \tag{6}$$

$$\mathrm{m}_1\cdot + \mathrm{m}_2\cdot \xrightarrow{k_{\mathrm{t}12}} \text{polymer} \tag{7}$$

$$\mathrm{m}_2\cdot + \mathrm{m}_2\cdot \xrightarrow{k_{\mathrm{t}22}} \text{polymer} \tag{8}$$

The overall copolymerization rate R_p is expressed as

$$R_\mathrm{p} = -\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])/\mathrm{d}t = k_{11}[\mathrm{m}_1\cdot][\mathrm{M}_1] + k_{12}[\mathrm{m}_1\cdot][\mathrm{M}_2] + k_{21}[\mathrm{m}_2\cdot][\mathrm{M}_1] \tag{9}$$

Applying the steady-state approximation expressed in eq

10 and 11, and introducing them to eq 9, we obtain eq 12.

$$k_{12}[\mathrm{m}_1\cdot][\mathrm{M}_2] = k_{21}[\mathrm{m}_2\cdot][\mathrm{M}_1] \quad (10)$$

$$R_\mathrm{i} = R_\mathrm{t} = k_{\mathrm{t}11}[\mathrm{m}_1\cdot]^2 + 2k_{\mathrm{t}12}[\mathrm{m}_1\cdot][\mathrm{m}_2\cdot] + k_{\mathrm{t}22}[\mathrm{m}_2\cdot]^2 \quad (11)$$

$(R_\mathrm{i}$ = initial rate)

$$R_\mathrm{p} = \frac{R_\mathrm{i}^{1/2}k_{21}(k_{11}[\mathrm{M}_1] + 2k_{12}[\mathrm{M}_2])[\mathrm{M}_1]}{(k_{\mathrm{t}11}k_{21}^2[\mathrm{M}_1]^2 + 2k_{\mathrm{t}12}k_{12}k_{21}[\mathrm{M}_1][\mathrm{M}_2] + k_{\mathrm{t}22}k_{12}^2[\mathrm{M}_2]^2)^{1/2}} \quad (12)$$

Assuming that the cross-termination rate is approximately the mean of the homotermination rates. We get

$$R_\mathrm{p} = \frac{R_\mathrm{i}^{1/2}(k_{11}[\mathrm{M}_1] + 2k_{12}[\mathrm{M}_2])}{k_{\mathrm{t}11}^{1/2} + k_{\mathrm{t}22}^{1/2}\dfrac{k_{12}}{k_{21}}\dfrac{[\mathrm{M}_2]}{[\mathrm{M}_1]}} \quad (13)$$

If the second term in the denominator is larger than the first, $(k_{\mathrm{t}22})^{1/2}k_{12}/k_{21} > 10(k_{\mathrm{t}11})^{1/2}$, eq 13 will be reduced to eq 14.

$$R_\mathrm{p} = \frac{R_\mathrm{i}^{1/2}}{(k_{\mathrm{t}22})^{1/2}}k_{21}\left(2 + \frac{k_{11}[\mathrm{M}_1]}{k_{12}[\mathrm{M}_2]}\right)[\mathrm{M}_1] \quad (14)$$

Equation 14 provides the copolymerization rates which fit the experimental data of the present copolymerization rates satisfactorily as shown in Figure 2, by applying the method of least squares. (In doing this, the value of 0.25 is used for k_{11}/k_{12}, which is obtained from Fineman–Ross plot in Figure 5.)

Thus, the present copolymerizations are explained in terms of the termination processes in which the contribution of the homotermination of VCZ radical species is negligibly small when compared with that of DEM or DMM radical species or with the cross-termination process, despite the fact that the Q values of these electron-accepting monomers are smaller than that of VCZ, that is, the growing chain radicals of these electron-accepting monomers appear to be less stable than VCZ radical species.

Acknowledgment. The authors are grateful to Professor M. Litt of Case Western Reserve University for his suggestion to use eq 13 which enabled them to include all three termination steps in the discussion.

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Polymerization of Phenylacetylenes. III. Structure and Properties of Poly(phenylacetylene)s Obtained by WCl_6 or $MoCl_5$

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ABSTRACT: Structure and properties of poly(phenylacetylene)s were investigated. The poly(phenylacetylene)s were obtained in the polymerization at 30° by WCl_6 or $MoCl_5$ in several solvents (C_6H_6, CCl_4, $CHCl_3$, and CH_2Cl_2). Molecular weights of the polymers were 5500–12000. The polymers produced by WCl_6 in polar solvents showed high softening points (~226°), a small absorption at 870 cm^{-1} in ir spectrum, and an emission at 430 nm by excitation at 250 nm; these were correlated with high content of trans structure. On the other hand, the polymers formed by $MoCl_5$ in nonpolar solvents showed low softening points (~215°), a large absorption at 870 cm^{-1}, and an emission at 360 nm, which were attributed to high content of cis structure. The numbers of unpaired spin of the polymers were in a range of 10^{16}–10^{17} spin g^{-1}, and the electric conductivities were 10^{-18}–10^{-15} $\mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$.

In a previous paper[1] we reported that phenylacetylene was polymerized by WCl_6 or $MoCl_5$ to produce poly(phenylacetylene)s with molecular weights of ca. 10000. The polymer produced was completely soluble in benzene. Little amount of methanol-soluble oligomer was formed. The effects of solvent and ring substituent on the polymerization of phenylacetylene were different from those observed in the cationic polymerization of styrene by WCl_6.[1,2]

Phenylacetylene has been reported to polymerize by coordination,[3-7] radical[8-10] or cationic[11,12] mechanism. Only oligomers with molecular weights of ca. 1000, however, are formed by radical or cationic mechanism. In coordination polymerizations, not only polymers with a molecular weight of several thousand but also benzene-insoluble polymers and methanol-soluble oligomers (including a cyclic trimer) are usually formed. Very recently, Woon and Farona[7] reported that phenylacetylene was polymerized by molybdenum complexes to yield high polymers.

The structure and properties of poly(phenylacetylene) have been investigated mainly with the samples produced by either Ziegler-Natta catalysts or thermal initiation. For example, Kern[4] synthesized cis- and trans-rich polymers, and examined their structure mainly by means of ir spectroscopy. Simionescu et al.[13] investigated the structure of poly(α-naphthylacetylene) in a similar manner. These studies were generally performed with fractional samples in coordination polymerization product, that is, with benzene-soluble and methanol-insoluble fractions. On the other hand, the polymerization of phenylacetylene by WCl_6 or $MoCl_5$ provides almost selectively benzene-soluble and