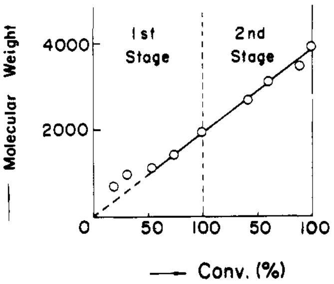

Figure 3. Plots of the conversion *vs.* molecular weight in the two-stage copolymerization of OXZ with PL.

dimethylformamide was subjected to the alternating copolymerization at 40°. After 10 hr when the conversions of both monomers were about 100%, the second feed of an equimolar mixture of the two monomers (each 7.5 mmol) in dimethylformamide (2 ml) was added to the system of the first polymerization mixture, and then, the system of the second-stage polymerization was kept at 40° for 10 hr. A plot of the conversion *vs.* molecular weight is shown in Figure 3. A linear relationship is observed. The straight line passes through the origin. In the first stage, however, the beginning in comparison with that at the latter stage This implies that the concentration of the macrozwitterion, *i.e.*, the molar concentration of copolymer, is lower at the beginning in comparison with that at the later stage where the concentration of macrozwitterion remains almost constant. After the concentration of **8** and/or **9** becomes greater betaine **7** reacts preferably with **8** or **9**, and the concentration of macrozwitterion does not increase. In the second stage, the macrozwitterion, whose concentration remains constant, continues to grow. The molecular weight at the end of the second stage is almost twice as high as that at the end of the first stage. The intermolecular and intramolecular reactions between the oxazolinium ring and carboxylate group at the macrozwitterions might take place during the polymerization. But the relationship of Figure 3 does not indicate the occurrence of the above reactions of the macrozwitterions under these conditions.

Table III
Copolymerization of OXZ with PL, MePL, and Me$_2$PL[a]

Comonomer	Time (hr)	Yield (%)	Mol Wt	Copolymer Composition (%) (OXZ–β-Lactone)
PL	25	61	3500	50–50[b]
MePL	27	42	4000	50–50[b]
Me$_2$PL	45	21	3610	44–56

[a] 7.5 mmol of each monomer in 2.0 ml of acetonitrile at 10–20°. [b] 1:1 alternating copolymer.

Copolymerization Reactivities of PL, MePL, and Me$_2$PL. The reactivities of PL, MePL, and Me$_2$PL were examined in the copolymerization with OXZ at lower temperatures. Table III shows the copolymerization results in acetonitrile at 10–20°. In all cases white powdery polymers were obtained. They are hygroscopic and soluble in acetonitrile, chloroform, dimethylformamide, methanol, and water.

The copolymerization reactivities are in a qualitative order of PL > MePL > Me$_2$PL. Introduction of methyl group to the α position of carbonyl group resulted in a decrease of copolymerization reactivities. This order agrees with that observed in the anionic homopolymerization of β-lactones,[3,4] in which the rate-determining step of the polymerization is the attack of the propagating carboxylate anion on the monomer accompanying the ring opening of β-lactone. The situation is quite similar to the copolymerization *via* betaine propagation, *e.g.*, the rate-determining step of the copolymerization in the present study is probably the formation of betaine **7** involving the ring opening of β-lactone by the nucleophic attack of OXZ as shown by eq 2.

Further studies on the betaine propagation are currently undertaken in our laboratory especially from the mechanistic point of view.

Mechanism of Charge-Transfer Polymerization. VI. Alternating Radical Copolymerization of *N*-Vinylcarbazole with Electron-Accepting Monomers[1]

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ABSTRACT: *N*-Vinylcarbazole was successfully copolymerized with such electron-accepting monomers as fumaronitrile or diethyl fumarate to give the 1:1 alternating copolymer regardless of the monomer feed composition under conditions of free radical initiation. Characterizations of the copolymers and comparable polymerization features between these two systems are described. A generalized mechanism involving participation of both the monomer charge-transfer complex and the free monomers is proposed for the alternating radical copolymerization.

There have been a number of studies on the alternating radical copolymerization in view of both synthetic and mechanistic interest. Especially, the propagation mechanism for the alternating radical copolymerization has long been the subject of controversy and is still left to be clarified. Numerous alternating radical copolymerization systems, either spontaneously initiated or initiated by a free-radical initiator, have been reported to date in the combinations of various olefins with maleic anhydride or sulfur dioxide in particular.[2-4] With respect to the *N*-vinylcarbazole (VCZ) monomer, which has recently received much

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(1) Part V of this series: K. Tada, Y. Shirota, and H. Mikawa, *J. Polym. Sci., Part A-1*, in press.

(2) For examples, see (a) M. C. deWilde and G. Smets, *J. Polym. Sci.*, **5**, 253 (1950); (b) D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.*, **55**, 1293 (1959); (c) M. M. Martin and N. P. Jensen, *J. Org. Chem.*, **27**, 1201 (1962); (d) S. Iwatsuki and Y. Yamashita, *Macromol. Chem.*, **89**, 205 (1965); (e) N. L. Zutty, C. W. Wilson, G. H. Potter, D. C. Priest, and C. J. Whitworth, *J. Polym. Sci., Part A*, **3**, 2781 (1965).

attention in the field of the charge-transfer polymerization, *i.e.*, the polymerization initiated by an electron acceptor, no alternating copolymerization has been known to date, although several nonalternating radical copolymerizations of VCZ have been reported with such comonomers as styrene, methyl methacrylate, methyl acrylate, or vinylidene chloride.[5] As a part of a series of our studies on the charge-transfer polymerization of VCZ,[1,6] we investigated free radical-initiated copolymerizations of VCZ with electron-accepting monomers with a hope that when suitable electron-accepting monomers are selected as comonomers, alternating copolymerizations might proceed, and that if so, the systems might provide helpful information on the mechanism of the alternating radical copolymerization. We report here the first successful alternating radical copolymerizations of VCZ with such electron-accepting monomers as fumaronitrile (FN) or diethyl fumarate (DEF).[7] A generalized mechanism involving participation of both the free monomers and the charge-transfer complex formed between the monomer pairs is proposed for the alternating radical copolymerization, and the rate features of the present systems are explained qualitatively in terms of this mechanism.

Experimental Section

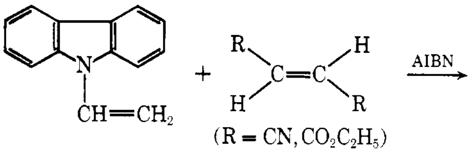
Materials. *N*-Vinylcarbazole (VCZ) was purified and dried as described before.[6a] Fumaronitrile (FN) of pure grade (Wako Pure Chemical Industries Ltd.) was recrystallized three times from benzene, fractionally sublimed twice in *vacuo*, stored, and resublimed immediately before use. Commercially available diethyl fumarate (DEF) of pure grade was first dried over calcium chloride and then fractionally distilled twice over calcium hydride in *vacuo* under a nitrogen stream, bp 75° (5 mm). 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized four times from methanol and dried in *vacuo*. Benzene was purified and dried in the usual way, and distilled twice from metallic sodium immediately before use. *N,N*-Dimethylformamide was dried over molecular sieves (Linde 4A) and fractionally distilled over calcium hydride under reduced pressure immediately before use.

Polymerization Procedure. All copolymerizations were carried out in a solution using AIBN as an initiator. The monomer feed ratio was varied widely for a fixed total monomer concentration. The total monomer concentration employed was 0.8, 1.0, or 2.0 *M*, and the catalyst concentration was 1×10^{-3} *M*. The solution of the monomers and the catalyst which was introduced in a glass tube was evacuated at 2×10^{-2} mm by several freeze-pump-thaw cycles and then sealed off with or without a flow of dry nitrogen gas. The polymerization system wrapped with aluminum foil to avoid exposure to light was allowed to stand for an appropriate time in a thermostat maintained at 60 ± 0.1 or 80 ± 0.1°. The polymerization was stopped at low conversions, *i.e.*, less than 10% at most. The copolymerization of the VCZ–DEF system proceeded homogeneously throughout the reaction. In the VCZ–FN system copolymers formed precipitated from the reaction solution as the polymerization proceeded in a benzene solution. The polymerization solution of the VCZ–DEF system was poured into a large volume of methanol to precipitate polymers, and that of the VCZ–FN system was first added with H_4furan to dissolve precipitated polymers, and then poured into a large volume of methanol. The polymers thus obtained were washed with methanol repeatedly, dried in *vacuo*, and weighed. The copolymer formation was accompanied by the formation of a very small or trace amount of VCZ homopolymer. The VCZ homopolymer and the copolymer were separated by fractionation with a solvent based on different solubility behaviors of these polymers; that is, the VCZ homopolymer was eliminated from the VCZ–FN copolymer by washing the polymers with benzene; the VCZ–DEF copolymer was separated from the VCZ homopolymer by dissolving the former in carbon tetrachloride. The VCZ–FN copolymer was twice reprecipitated from H_4furan with methanol, and the VCZ–DEF copolymer from benzene with methanol, and they were submitted to analyses.

Apparatus. Ir spectra were taken with Hitachi EPI-G2 and Jasco Ir-G infrared spectrophotometers. Uv spectra were taken with a Hitachi 124 spectrophotometer. Emission spectra were recorded with a Hitachi MPF Model 3 spectrophotofluorometer. Molecular weights were determined with a Mechrolab VPO Model 302.

Results and Discussion

N-Vinylcarbazole was successfully copolymerized with such electron-accepting monomers as FN or DEF in a benzene solution at 60 or 80° under initiation with AIBN to generate the 1:1 alternating copolymer regardless of the monomer feed composition. In both systems the copolymer formed preferentially with simultaneous formation of a very small or trace amount of VCZ homopolymer. It should be noted here that in the absence of AIBN cationic polymerization of VCZ was initiated by these electron-accepting monomers (above 10 mol % concentration to VCZ), FN being a much stronger cationic initiator than DEF.[8]



1:1 alternating copolymer

Various 1:1 alternating copolymers have been prepared to date, however, the preparation of the 1:1 alternating copolymer containing as one component vinyl monomers possessing large π-electron aromatic rings as pendant groups has not been reported as far as we know. The present successful syntheses of the 1:1 alternating copolymers containing VCZ as one component provide the example. These copolymers are of interest in that they serve as excellent model compounds for the study of the excimer state of $(VCZ)_n$ which has recently received attention.[9,10]

Characterization of Copolymers. The copolymer formation was confirmed by the solubility behaviors, elementary analyses, and ir and uv spectra of the copolymers which were reprecipitated repeatedly. Both copolymers, VCZ–FN and VCZ–DEF, were obtained as white powders.

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(3) Furthermore, a number of alternating copolymerizations have recently been reported between various olefins and polar monomers complexed with the metal halides.[4]

(4) For examples, see (a) N. G. Gaylord, *J. Polym. Sci., Part C*, **31**, 247 (1970); (b) N. G. Gaylord and B. Matyska, *J. Macromol. Sci. Chem., Part A*, **4**, 1507 (1970), and references cited therein.

(5) R. Hart, *Macromol. Chem.*, **47**, 143 (1961).

(6) (a) Part I: T. Natsuume, M. Nishimura, M. Fujimatsu, M. Shimizu, Y. Shirota, H. Hirata, S. Kusabayashi, and H. Mikawa, *Polym. J.*, **1**, 181 (1970); (b) part II: M. Fujimatsu, T. Natsuume, H. Hirata, Y. Shirota, S. Kusabayashi, and H. Mikawa, *J. Polym. Sci., Part A1*, **8**, 3349 (1970); (c) part III: Y. Shirota, K. Kawai, N. N. Yamamoto, K. Tada, T. Shida, H. Mikawa, and H. Tsubomura, *Bull. Chem. Soc. Jap.*, **45**, 2683 (1972); part IV: K. Tada, Y. Shirota, and H. Mikawa, *Macromolecules*, **6**, 9 (1973).

(7) A part of the results has been reported in previous communications: (a) Y. Shirota, A. Matsumoto, and H. Mikawa, *Polym. J.*, **3**, 643 (1972); (b) M. Yoshimura, Y. Shirota, and H. Mikawa, *J. Polym. Sci., Part B*, 457 (1973).

(8) M. Nishimura, A. Matsumoto, Y. Shirota, S. Kusabayashi, and H. Mikawa, Presented at the 19th Symposium on Macromolecular Chemistry, Reprint 21A05, 1970, p 117; papers in preparation.

(9) (a) W. Klopffer, *J. Chem. Phys.*, **50**, 2337 (1969); (b) P. C. Johnson and H. W. Offen, *J. Chem. Phys.*, **55**, 2945 (1971); (c) Y. Nishijima, Y. Sasaki, K. Hirota, and M. Yamamoto, *Rept. Progr. Polym. Phys. Jap.*, **15**, 449 (1972); (d) C. David, M. Piens, and G. Geuskens, *Eur. Polym. J.*, **8**, 1019 (1972).

(10) In contrast to the VCZ homopolymer and some copolymers of VCZ, these 1:1 alternating copolymers were found to exhibit only the monomeric fluorescence due to the pendant carbazyl group in a solution over a wide range of temperature (see Figure 2). It was indicated from this fact coupled with the evidence of the occurrence of energy transfer in these alternating copolymers that the excimer state of $(VCZ)_n$ is formed only by the interaction of the nearest carbazyl groups. M. Atsumi, T. Tamamura, M. Yokoyama, M. Yoshimura, Y. Shirota, and H. Mikawa, Presented at the 22nd Annual Meeting on Macromolecular Chemistry, Reprint 1, 29C10, 1973, p 68.

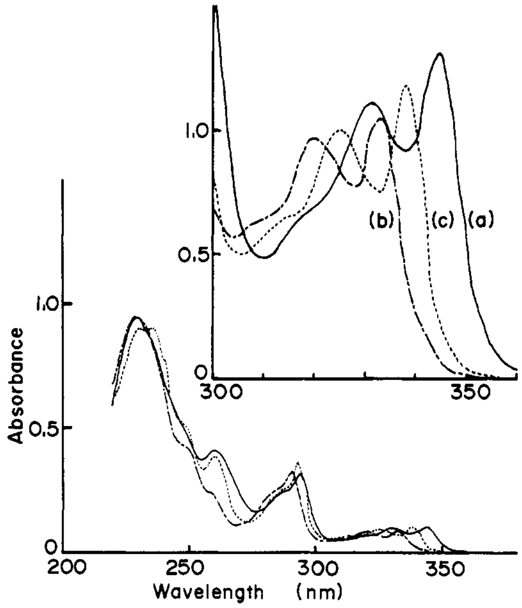


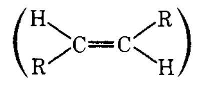
Figure 1. Electronic absorption spectra of $(VCZ)_n$, and VCZ-FN and VCZ-DEF 1:1 alternating copolymers in H_4furan: (a) --, $(VCZ)_n$; (b) -----, VCZ-FN copolymer; (c) ------, VCZ-DEF copolymer. Concentration: $[(VCZ)_n] = 4.5 \times 10^{-4}$ *M* (above), 3.19×10^{-5} *M* (below); [VCZ-FN copolymer] = 2.20 mg/25 ml solution (above), 1/12.5 concentration of the above (below); [VCZ-DEF copolymer] = 2.54 mg/25 ml solution (above), 1/12.5 concentration of the above (below).

Table I
Compositions and Molecular Weights of the Copolymers

Mol Fraction of VCZ in Monomer Feed	N Content in Copolymer (%)		Mol Fraction of VCZ in Copolymer		Mol Wt[a]
	I. VCZ–FN Copolymer[b]				
	A	B	A	B	
0.9	14.83	14.07	0.53	0.56	7,680
0.8	13.97	14.82	0.57	0.53	8,050
0.7	14.16	14.63	0.56	0.54	8,110
0.6	14.75	14.12	0.53	0.56	10,580
0.5	14.67	14.05	0.54	0.56	6,190
0.4	14.27	14.61	0.55	0.54	6,180
0.3	13.74	14.80	0.58	0.53	6,420
0.2	14.25	14.89	0.55	0.52	5,530
0.1		14.64		0.54	
	II. VCZ–DEF Copolymer[c]				
	C	D	C	D	
0.9	4.10	3.90	0.54	0.51	18,600
0.8	4.04	3.95	0.53	0.51	16,700
0.7	4.01	4.11	0.53	0.54	15,980
0.6	4.10	3.67	0.54	0.48	15,890
0.5	3.87	3.67	0.50	0.48	13,810
0.4	3.89	3.69	0.51	0.48	13,240
0.3	3.83	3.69	0.50	0.48	11,370
0.2	3.80		0.50		
0.1	3.62		0.47		

[a] Molecular weights were determined with respect to the copolymer A and C for the VCZ–FN and VCZ–DEF copolymer, respectively. [b] Copolymers A and B were obtained under the following reaction conditions: A, [VCZ] + [FN] = 0.8 *M*; [AIBN] = 1×10^{-3} *M*; solvent, benzene; temperature, 60°; time, 30 min; B, [VCZ] + [FN] = 2.0 *M*; other conditions, the same with the above. [c] Copolymers C and D were obtained under the following reaction conditions; C, [VCZ] + [DEF] = 1.0 *M*; [AIBN] = 1×10^{-3} *M*; solvent, benzene; temperature, 80°; time, 30 min; D, solvent, *N,N*-dimethylformamide; other conditions, the same with the above.

While the VCZ-DEF copolymers softened at between 180 and 230°, the VCZ-FN copolymers did not soften below 300°. The VCZ-FN copolymers are entirely insoluble in benzene, but soluble in H_4furan, *N,N*-dimethylformamide, and Me_2SO, partly soluble in acetone, while VCZ homopolymer is easily soluble in benzene as well as in H_4furan, *N,N*-dimethylformamide, or Me_2SO, but difficultly soluble in acetone. The solubility behaviors of the VCZ-DEF copolymers are similar to those of VCZ homopolymer, but the copolymers can be dissolved in CCl_4 in which VCZ homopolymer is almost insoluble. The number-average molecular weights of the copolymers obtained in a benzene solution were in the ranges 5500–11,000 and 10,000–18,700 with the VCZ-FN and VCZ-DEF copolymers, respectively (Table I). It was found that the largeness of the molecular weight of the copolymers obtained for various monomer feed ratios was in parallel with the largeness of the polymerization rate described later. Thus, the value of the molecular weight obtained for the VCZ-DEF copolymers increased monotonously with the increase in the VCZ molar ratio in the monomer feed. The largest value of the molecular weight for the VCZ-FN copolymers was found at a higher molar ratio of VCZ in the monomer feed. The ir spectra of the VCZ-FN and VCZ-DEF copolymers show a weak C≡N absorption at 2250 cm^{-1}, a strong C=O absorption at 1740 cm^{-1}, respectively. The characteristic ir absorption peaks at 963 and 866 cm^{-1} due to the terminal vinyl group on a nitrogen atom observed in the VCZ monomer and those at 965 and 975 cm^{-1} due to the trans out-of-plane C—H deformation vibration



observed in FN and DEF monomers, respectively, essentially disappeared in the copolymers. It is indicated that the copolymerization proceeded at the olefinic double bonds of both monomers. The copolymer composition was found to be constantly 1:1 from the nitrogen analysis, irrespective of the widely varied monomer feed ratios in both copolymers. The results are summarized in Table I. From this result together with the fact that the FN or DEF monomer did not homopolymerize under the present reaction conditions, the copolymers were assigned as the 1:1 alternating copolymer between VCZ and FN or DEF.[11] Noticeably, these 1:1 alternating copolymers are characteristic in their electronic absorption spectra. The lower energy π–π^* absorption maxima observed at 344 and 330 nm in VCZ homopolymer shifted toward the blue region by about 10 nm in the VCZ-FN copolymer (λ_{max} 333 and 320 nm) and 5 nm in the VCZ-DEF copolymer (λ_{max} 338.5 and 325 nm), although the wavelength of the higher energy absorption maxima were similar between $(VCZ)_n$ and the copolymers (Figure 1). The extent of the blue shift of the lower energy π–π^* absorption maxima due to the carbazyl moiety in the copolymers of VCZ appears to be dependent on the electron-accepting strength of the comonomer in the monomer state. Copolymers of VCZ with styrene containing appreciable amounts of VCZ were found to show almost identical π–π^* absorption due to the carbazyl moiety with that of $(VCZ)_n$, and the similar is reported with VCZ-methyl methacrylate copolymers.[12] The fluorescence emission

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(11) A possibility that the material is a homopolymer of VCZ with the FN or DEF monomer strongly complexed 1:1 to each recurring unit is denied from the ir and uv spectrophotometric data. Also, an attempt to prepare the above complex was made by adding FN or DEF into a benzene solution of $(VCZ)_n$ and then precipitating with methanol with or without heat, but in fail.

(12) A. V. Chernobai, A. I. Shepelva, and V. S. Zubkova, *Vysokomolekul. Soedin.*, 7, 1080 (1965); *Chem. Abstr.*, 63, 10080*h* (1965).

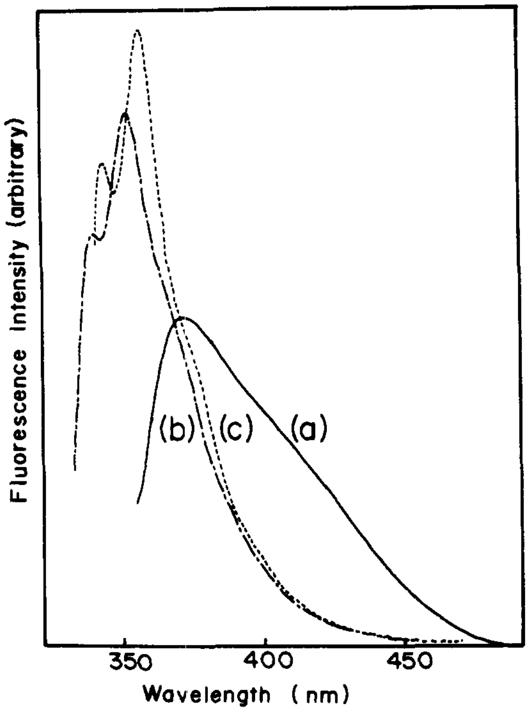

Figure 2. Fluorescence emission spectra of $(VCZ)_n$, and VCZ-FN and VCZ-DEF 1:1 alternating copolymers in H_4furan: (a) ——, $(VCZ)_n$, concentration 3.98×10^{-4} *M*, excitation wavelength 344 nm; (b) -----, VCZ-FN copolymer, concentration 2.0 mg/25 ml solution, excitation wavelength 333 nm; (c) ------, VCZ-DEF copolymer, concentration 2.0 mg/25 ml solution, excitation wavelength 338 nm.

spectra of $(VCZ)_n$ and the copolymers are shown in Figure 2.

Rate Features and the Charge-Transfer Interaction. The VCZ-FN and VCZ-DEF 1:1 alternating copolymerization systems showed different rate features with each other. When the initial rates of copolymerization were plotted against the monomer feed ratios, the maximum rate was found at a higher VCZ content in the monomer feed in the VCZ-FN system: the maximum point of the rate was found at the molar ratio of 7:3 (VCZ:FN) in the monomer feed for a constant total monomer concentration of 0.8 *M* in a benzene solution. As the total monomer concentration increased to *e.g.*, 2.0 *M*, the maximum point of the rate appeared to show slight shift toward the monomer feed ratio of unity (1:1). The results are shown in Table II and Figure 3. By contrast, in the VCZ-DEF system no maximum phenomenon of the rate was apparent and the rate increased almost linearly with the increase in the VCZ content in the monomer feed under similar reaction conditions as shown in Table III and Figure 4. It should be pointed out that the rates of the copolymerization of the VCZ-FN system were approximately five to twenty times faster than those of the VCZ-DEF system under similar reaction conditions.

Formation of the charge-transfer complex between the monomer pairs was confirmed spectroscopically in the present alternating copolymerization systems. The solution of VCZ and FN or DEF was pale yellow or slightly yellow colored, the coloration being stronger with FN than with DEF. Although no distinct charge-transfer band was observed in both systems, the absorption spectra of these systems shifted to the red region as compared with the sum of the absorptions of VCZ and FN or DEF of the same concentration. A continuous variation method applied to the absorption due to the charge-transfer interaction revealed that in both systems the 1:1 charge-transfer complex is formed between VCZ and FN or DEF in the ground state as shown in Figures 5 and 6.

Table II
Initial Copolymerization Rates (R_p) in the VCZ-FN System[a]

Mol Fraction of VCZ in Monomer Feed	Monomer Feed (mg) VCZ	Monomer Feed (mg) FN	Polymer Yield (mg)	R_p[b] ($\times 10^{-4}$ mol/l. min)
	I. [VCZ] + [FN] = 0.8 *M*[c]			
1.0	772.0	0	88.0	30.3
0.9	694.8	31.2	57.2	14.1
0.8	617.6	62.4	74.6	18.3
0.7	540.4	93.6	85.9	21.1
0.6	463.2	124.8	82.3	20.2
0.5	386.0	156.0	74.4	18.3
0.4	308.8	187.2	65.4	16.1
0.3	231.6	218.4	51.5	12.7
0.2	154.4	249.6	37.8	9.3
	II. [VCZ] + [FN] = 2.0 *M*			
0.9	1737	78	152.2	37.3
0.8	1544	156	195.6	47.9
0.7	1351	234	197.8	48.6
0.6	1158	312	212.5	52.2
0.5	965	390	204.9	50.4
0.4	772	468	171.9	42.2
0.3	579	546	140.6	34.5
0.2	386	624	107.2	26.3
0.1	193	702	48.5	11.9

[a] Reaction conditions: [AIBN] = 1×10^{-3} *M*; solvent, benzene (5 ml); temperature, 60°; polymerization time, 30 min. [b] $R_p = d[P]/dt = -(1/2)(d/dt)([M_1] + [M_2])$ for the $VCZ(M_1)$-$FN(M_2)$ and $VCZ(M_1)$-$DEF(M_2)$ 1:1 alternating copolymerization; P represents polymer; $R_p = d[P]/dt = -(d/dt)[M_1]$ for the homopolymerization of VCZ. [c] No value was detected for a mole fraction of 0.1.

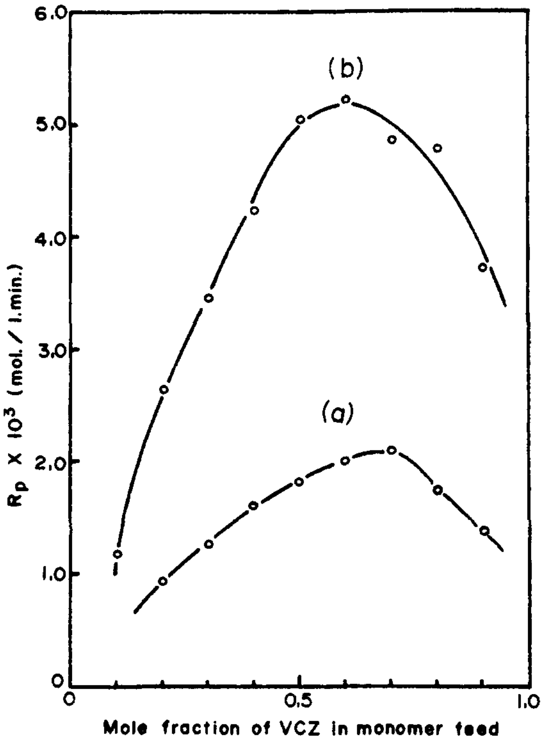

Figure 3. Initial copolymerization rates *vs.* monomer feed molar ratios in the VCZ-FN system. [AIBN] = 1×10^{-3} *M*; temperature, 60°; solvent, benzene: (a) [VCZ] + [FN] = 0.8 *M*; (b) [VCZ] + [FN] = 2.0 *M*.

A Proposed Mechanism for the Alternating Radical Copolymerization. The principal mechanisms hitherto proposed involve the cross-propagation of the free monomers in which the transition state is stabilized either by

Table III
Initial Copolymerization Rates (R_p) in the VCZ–DEF System[a]

Mol Fraction of VCZ in Monomer Feed	Monomer Feed (mg)		Polymer Yield (mg)	R_p[b] ($\times 10^{-4}$ mol/l. min)
	VCZ	FN		
		I. At 60°		
1.0[c]	482.5	0	73.8	50.9
0.9	868.5	86.0	15.1	2.75
0.8	772.0	172.0	12.9	2.35
0.7[d]	675.0	258.0	11.8	2.15
0.6	579.0	344.0	8.9	1.62
0.5	482.5	430.0	7.8	1.42
0.4	386.0	516.0	7.3	1.33
0.3	289.5	602.0	6.2	1.13
0.2	193.0	688.0	3.8	0.69
0.1	96.5	774.0	1.7	0.31
		II. At 80°[e]		
1.0	482.5	0	231.8 (–)	160.1 (–)
0.9	868.5	86.0	85.1 (67.4)	15.5 (12.2)
0.8	772.0	172.0	75.8 (59.3)	13.8 (10.8)
0.7	675.0	258.0	63.1 (52.0)	11.5 (9.5)
0.6	579.0	344.0	48.8 (38.7)	8.9 (7.0)
0.5	482.5	430.0	38.0 (31.8)	6.9 (5.8)
0.4	386.0	516.0	28.0 (23.5)	5.1 (4.3)
0.3	289.5	602.0	17.3 (14.0)	3.1 (2.5)
0.2	193.0	688.0	15.9 (5.7)	2.9 (1.0)
0.1	96.5	774.0	6.2 (–)	1.1 (–)

[a] Reaction conditions: [VCZ] + [DEF] = 1.0 *M*; [AIBN] = 1×10^{-3} *M*; solvent, benzene (5 ml)]; polymerization time, 30 min. [b] See Table II, footnote *b*. [c] Solvent, benzene (2.5 ml). [d] [VCZ] = 0.7 *M* (675 mg), [DEF] = 0.5 *M* (430 mg); polymer yield (30 min), 10.9 mg; R_p ($\times 10^{-4}$ mol/l. min) = 1.98. [VCZ] = 0.7 *M* (675 mg), [DEF] = 0.7 *M* (602 mg); polymer yield (30 min), 13.0 mg; R_p ($\times 10^{-4}$ mol/l. min) = 2.35. [e] The value in the parentheses are the ones obtained in *N*,*N*-dimethylformamide.

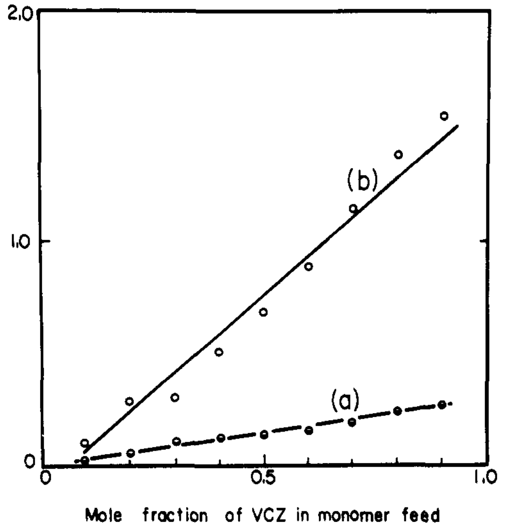

Figure 4. Initial copolymerization rates *vs.* monomer feed molar ratios in the VCZ-DEF system. [VCZ] + [DEF] = 1.0 *M*; [AIBN] = 1×10^{-3} *M*; solvent, benzene: (a) at 60°; (b) at 80°.

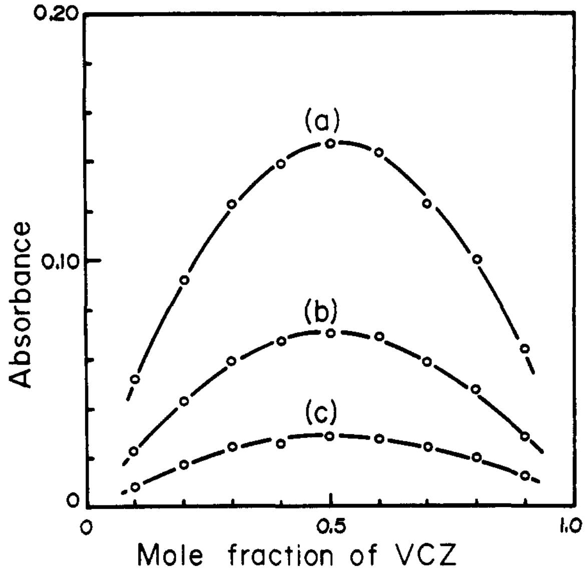

Figure 5. Continuous variation method applied to the charge-transfer absorption in the VCZ-FN system. [VCZ] + [FN] = 0.1 *M*; solvent, benzene; temperature, 25°: (a) measured at 390 nm; (b) at 400 mm; (c) at 410 nm.

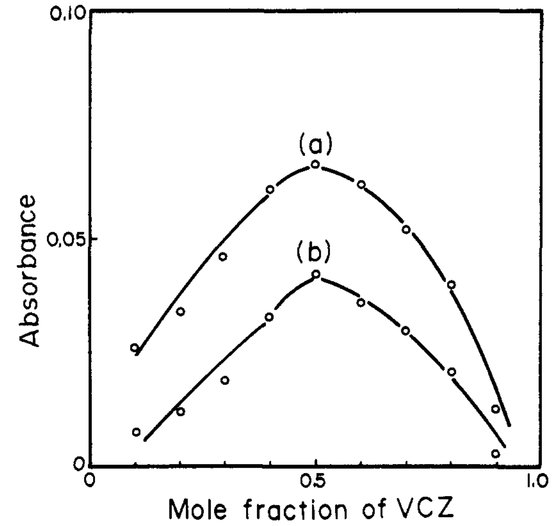

Figure 6. Continuous variation method applied to the charge-transfer absorption in the VCZ-DEF system. [VCZ] + [DEF] = 0.1 *M*; solvent, benzene; temperature, 23°. (a) measured at 370 nm; (b) at 380 nm.

electrostatic interaction[13] or by electron transfer[14] between propagating chain radicals and monomers, and the homopolymerization of the monomer charge-transfer complex, *i.e.*, the charge-transfer complex formed between the monomer pairs.[15] Yamashita and his coworkers favored the latter mechanism, that is, the monomer charge-transfer complex polymerizes as one unit to generate the 1:1 alternating copolymer, based on the results of especially the terpolymerization studies.[16,17] If this mechanism holds, the rate of copolymerization should maximize at the monomer feed molar ratio of unity (1:1) for a fixed total monomer concentration.[18] The rate features found for the present VCZ-FN and VCZ-DEF systems, however, are inconsistent with the mechanism of homopolymerization of the monomer charge-transfer complex.[19,20]

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(13) C. C. Price and T. Alfrey, Jr., *J. Polym. Sci.*, **1**, 83 (1946).

(14) C. Walling, E. A. Briggs, K. B. Wolfstrin, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1537 (1948).

(15) P. D. Bartlett and K. Nozaki, *J. Amer. Chem. Soc.*, **68**, 1495 (1946).

(16) (a) T. Kokubo, S. Iwatsuki, and Y. Yamashita, *Macromolecules*, **1**, 482 (1968); (b) T. Kokubo, S. Iwatsuki, and Y. Yamashita, *ibid.*, **3**, 518 (1970).

(17) Gaylord also proposed the concept of the homopolymerization of the monomer charge-transfer complex for the 1:1 alternating copolymerization, which is unique in that conventional radical species is not involved.

(18) When the bimolecular termination of the growing chain radicals is assumed, the polymerization rate R_p is simply expressed as

$$R_p = KR_i^{1/2}[C] \approx kR_i^{1/2}K[M_1][M_2]$$

where *k* is the constant, *K* is the equilibrium constant for the formation of the charge-transfer complex, and R_i is the rate of initiation.

We propose here a generalized mechanism for the alternating radical copolymerization, which involves participation of both the monomer charge-transfer complex and the free monomers in the propagation process of the polymerization. Participation of the monomer charge-transfer complex to the polymerization has recently been supported in many studies.[16,20,21] We consider that the degree of the contribution of each of them varies greatly depending upon the reaction system. The reaction condition may also affect the degree of their contributions. Thus, such extreme cases may exist as in one system the monomer charge-transfer complex contributes overwhelmingly to the propagation step of the polymerization, or in another system, on the contrary, the polymerization involves the reactions of almost only the free monomers. The following four processes (1-4) are considered in the propagation process.

Propagation process

$$\mathrm{m_1\cdot} + \mathrm{M_2} \xrightarrow{k_{12}} \mathrm{m_2\cdot} \qquad (1)$$

$$\mathrm{m_2\cdot} + \mathrm{M_1} \xrightarrow{k_{21}} \mathrm{m_1\cdot} \qquad (2)$$

$$\mathrm{m_2\cdot} + \mathrm{M_2M_1} \xrightarrow{k_{1c}} \mathrm{m_1\cdot} \qquad (3)$$

$$\mathrm{m_1\cdot} + \mathrm{M_1M_2} \xrightarrow{k_{2c}} \mathrm{m_2\cdot} \qquad (4)$$

The reactions of the free monomers M_1 and M_2 are expressed as eq 1 and 2; here only cross-reactions occur until either of the monomers is consumed even if each or either of the monomers can homopolymerize. The reactions of the monomer charge-transfer complex M_1M_2 (or M_2M_1) are expressed as eq 3 and 4; here the complex is attacked in its both sides by the propagating chain radicals $m_1\cdot$ or $m_2\cdot$ in such a way as M_1 side of the complex is attacked preferentially by $m_2\cdot$ and M_2 side of the complex by $m_1\cdot$. The initiation process and the termination one in which bimolecular reactions of the propagating chain radicals are assumed may generally involve the following competitive reactions as shown in eq 5-8 and 9-11, respectively.

Initiation process

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R\cdot} \quad \text{(initiator decomposition)}$$

$$\mathrm{R\cdot} + \mathrm{M_1} \xrightarrow{k_{i1}} \mathrm{m_1\cdot} \qquad (5)$$

$$\mathrm{R\cdot} + \mathrm{M_2} \xrightarrow{k_{i2}} \mathrm{m_2\cdot} \qquad (6)$$

$$\mathrm{R\cdot} + \mathrm{M_2M_1} \xrightarrow{k_{ic1}} \mathrm{m_1\cdot} \qquad (7)$$

$$\mathrm{R\cdot} + \mathrm{M_1M_2} \xrightarrow{k_{ic2}} \mathrm{m_2\cdot} \qquad (8)$$

Termination process

$$\mathrm{m_1\cdot} + \mathrm{m_1\cdot} \xrightarrow{k_{t11}} \text{polymer} \qquad (9)$$

$$\mathrm{m_1\cdot} + \mathrm{m_2\cdot} \xrightarrow{k_{t12}} \text{polymer} \qquad (10)$$

$$\mathrm{m_2\cdot} + \mathrm{m_2\cdot} \xrightarrow{k_{t22}} \text{polymer} \qquad (11)$$

The overall copolymerization rate R_p is the sum of the rate of reactions of the free monomers, $R_{p(f)}$, and that of reactions of the monomer charge-transfer complex, $R_{p(c)}$, and is expressed as

$$R_p = -(\mathrm{d}/\mathrm{d}t)([\mathrm{M_1}] + [\mathrm{M_2}]) = R_{p(f)} + R_{p(c)}$$
$$= k_{12}[\mathrm{m_1\cdot}][\mathrm{M_2}] + k_{21}[\mathrm{m_2\cdot}][\mathrm{M_1}] + k_{1c}[\mathrm{m_1\cdot}][\mathrm{C}] + k_{2c}[\mathrm{m_2\cdot}][\mathrm{C}] \qquad (12)$$

where $[M_1]$, $[M_2]$, and $[C]$ represent the concentration of the free monomers M_1 and M_2, and the monomer charge-transfer complex M_1M_2 (or M_2M_1), respectively, and $[m_1\cdot]$ and $[m_2\cdot]$ represent the ones of the growing chain radicals with the M_1 and M_2 end, respectively. The chain transfer reactions are neglected here for the sake of convenience. Since the equilibrium constant K for the formation of the charge-transfer complex is generally small in the alternating radical copolymerization system, eq 13

$$[\mathrm{C}] \approx K[\mathrm{M_1}][\mathrm{M_2}] \qquad (13)$$

holds. Applying the steady-state approximation, *i.e.*, eq 14 and 15, and introducing them into eq 12, we obtain a general rate equation for the alternating radical copolymerization (eq 16).

$$k_{12}[\mathrm{m_1\cdot}][\mathrm{M_2}] = k_{21}[\mathrm{m_2\cdot}][\mathrm{M_1}] \qquad (14)$$

$$R_i = R_t = k_{t11}[\mathrm{m_1\cdot}]^2 + 2k_{t12}[\mathrm{m_1\cdot}][\mathrm{m_2\cdot}] + k_{t22}[\mathrm{m_2\cdot}]^2 \qquad (15)$$

$$R_p = 2k_{21}[\mathrm{m_2\cdot}][\mathrm{M_1}] + \left(k_{2c} + \frac{k_{1c}k_{21}}{k_{12}}\frac{[\mathrm{M_1}]}{[\mathrm{M_2}]}\right)[\mathrm{m_2\cdot}][\mathrm{C}] = \frac{2k_{21}k_{12}[\mathrm{M_1}][\mathrm{M_2}]R_i^{1/2}}{(k_{t11}k_{21}^2[\mathrm{M_1}]^2 + 2k_{t12}k_{21}k_{12}[\mathrm{M_1}][\mathrm{M_2}] + k_{t22}k_{12}^2[\mathrm{M_2}]^2)^{1/2}} + \frac{\left(k_{2c} + \frac{k_{1c}k_{21}}{k_{12}}\frac{[\mathrm{M_1}]}{[\mathrm{M_2}]}\right)Kk_{12}[\mathrm{M_1}][\mathrm{M_2}]^2R_i^{1/2}}{(k_{t11}k_{21}^2[\mathrm{M_1}]^2 + 2k_{t12}k_{21}k_{12}[\mathrm{M_1}][\mathrm{M_2}] + k_{t22}k_{12}^2[\mathrm{M_2}]^2)^{1/2}} \qquad (16)$$

where R_i is the rate of initiation.

Here let us consider the following two extreme cases. It must be noted that the rate features of the copolymerization can generally be understood as the overlap of the independent rate features of the following two extreme cases. Case 1: when the concentration of the monomer charge-transfer complex is too low, and thus the reaction of the complex can almost be negligible, the rate R_p will become nearly equal to $R_{p(f)}$, the rate considering only the cross-propagation of the free monomers as expressed in eq 17;[22] in this case the rate of copolymerization will

case 1

$$R_p \approx R_{p(f)} = \frac{2k_{21}k_{12}[\mathrm{M_1}][\mathrm{M_2}]R_i^{1/2}}{(k_{t11}k_{21}^2[\mathrm{M_1}]^2 + 2k_{t12}k_{21}k_{12}[\mathrm{M_1}][\mathrm{M_2}] + k_{t22}k_{12}^2[\mathrm{M_2}]^2)^{1/2}} \qquad (17)$$

maximize at the monomer feed composition of 1:1 (molar ratio) only when the termination occurs by the cross-reaction between $m_1\cdot$ and $m_2\cdot$ for a constant rate of initiation. Case 2: when the concentration of the monomer charge-transfer complex is relatively high and its reactivity is very much activated, and thus the monomer charge-transfer complex contributes overwhelmingly to the polymerization, the rate R_p will become nearly equal to $R_{p(c)}$, which will be reduced to either eq 18 or 19;[23] the rate equation is not symmetrical with respect to $[M_1]$ and $[M_2]$

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(19) The observation that the rate of the alternating radical copolymerization does not maximize at the monomer feed molar ratios of 1:1 has also been reported in the systems styrene-maleic anhydride or 2-chloroethyl vinyl ether-maleic anhydride by Tsuchida and his coworkers,[20] who proposed the following mechanism for the polymerization: $m_1\cdot + C \rightarrow m_1\cdot$, $m_1\cdot + M_2 \rightarrow m_2\cdot$, $m_2\cdot + C \rightarrow m_1\cdot + M_2$, where M_1, M_2, free monomers; C, monomer charge-transfer complex; $m_1\cdot$, $m_2\cdot$, growing chain radical.

(20) (a) E. Tsuchida and T. Tomono, *Macromol. Chem.*, 141, 265 (1971); (b) E. Tsuchida, T. Tomono, and H. Sano, *Kogyo Kagaku Zasshi*, 73, 2031 (1970).

(21) J. A. Seiner and M. Litt, *Macromolecules*, 4, 308, 312 (1971).

(22) M. G. Baldwin, *J. Polym. Sci., Part A*, 3, 703 (1965).

(23) The second term can be negligible with respect to the first term since the former contains the quantity $k_{21}[m_2\cdot][M_1]$, which is nearly zero.

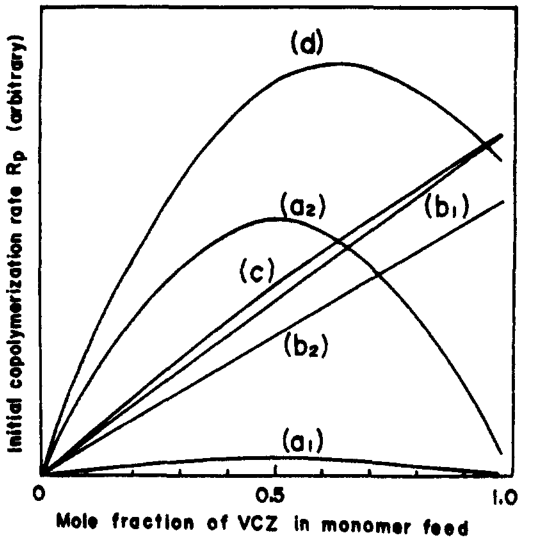

Figure 7. Expected rate features for the present alternating radical copolymerizations: initial copolymerization rates *vs.* monomer feed molar ratios.

so long as the turnovers of the growing chain radicals, *i.e.*, $m_1\cdot \rightarrow m_2\cdot$ and $m_2\cdot \rightarrow m_1\cdot$ are regulated by eq 14, although the contribution of these processes to the overall rate is very small.

case 2

$$R_p \approx R_{p(c)} = \left(k_{2c} + \frac{k_{1c}k_{21}}{k_{12}}\frac{[M_1]}{[M_2]}\right)[m_2\cdot][C] \approx k_{2c}[m_2\cdot][C] = \frac{k_{2c}k_{12}K[M_1][M_2]^2R_i^{1/2}}{(k_{t11}k_{21}^2[M_1]^2 + 2k_{t12}k_{21}k_{12}[M_1][M_2] + k_{t22}k_{12}^2[M_2]^2)^{1/2}} \quad (18)$$

or

$$R_p \approx \frac{k_{1c}k_{21}K[M_1]^2[M_2]R_i^{1/2}}{(k_{t11}k_{21}^2[M_1]^2 + 2k_{t12}k_{21}k_{12}[M_1][M_2] + k_{t22}k_{12}^2[M_2]^2)^{1/2}} \quad (19)$$

In addition, the most extreme situation of the case 2 is that reactions of the free monomers can completely be neglected, namely, the turnovers of the growing chain radicals do not occur, and only processes 3 and 4 take place in parallel or possibly either of processes 3 and 4 takes place preferentially. In this case we obtain rate eq 21, which is symmetrical with respect to $[M_1]$ and $[M_2]$, by assuming that the rate of process 3 is α times faster than that of process 4 and using eq 15. It is shown that the maximum rate always occurs at the monomer feed composition of 1:1 (molar ratio). Preferential occurrence of either process between 3 and 4 corresponds to the concept of the hitherto proposed homopolymerization mechanism of the monomer charge-transfer complex.

$$k_{1c}[m_1\cdot][C] = \alpha k_{2c}[m_2\cdot][C] \quad (20)$$

$$R_p = (1 + \alpha)k_{2c}[m_2\cdot][C] = \frac{(1 + \alpha)k_{2c}R_i^{1/2}K[M_1][M_2]}{\{k_{t11}(\alpha k_{2c}/k_{1c})^2 + 2k_{t12}(\alpha k_{2c}/k_{1c}) + k_{t22}\}^{1/2}} \quad (21)$$

Now, let us explain the rate features of the present VCZ(M_1)-FN(M_2) and VCZ(M_1)-DEF(M_2) systems in terms of the above-generalized mechanism. The following points should first be noted concerning these systems: (a) the M_1 monomer can homopolymerize, but the M_2 monomer does not homopolymerize under the present reaction conditions; (b) 1:1 alternating copolymers are always generated despite the fact that the M_1 monomer can homopolymerize, therefore, the relationship $k_{11} \ll k_{12}$ holds, where k_{11} represents the rate constant for the addition of $m_1\cdot$ to the M_1 monomer; (c) the rate of homopolymerization of VCZ is, however, faster or at least of comparable order of magnitude as compared with the rates of copolymerizations of VCZ-DEF or VCZ-FN systems, respectively (Tables II and III); therefore, the k_{21} process may be much slower (rate determining) than the k_{12} process. Accordingly, it can reasonably be indicated that in the present systems the rate constant k_{12} is much greater than the rate constant k_{21}, and likewise k_{1c} is probably greater than k_{2c}. This means that the $m_2\cdot$, *i.e.*, FN or DEF radical species, is much more stable, thus much less reactive than the $m_1\cdot$, *i.e.*, VCZ radical species, probably due to the more resonance stabilization in the former radical species, which is also reflected in their *Q* values. It is then suggested that the concentration of $m_1\cdot$ would be very small as compared with that of $m_2\cdot$ in the polymerization system under the steady-state conditions; therefore, most termination would be by coupling of like radicals, *i.e.*, $m_2\cdot$ in the present systems. Under these situations, the rate equation of the present systems can be reduced to eq 22 and 23 in the case 1 and case 2, respectively.

case 1

$$R_p = \frac{2k_{21}R_i^{1/2}}{(k_{t22})^{1/2}}[M_1] \quad (22)$$

case 2

$$R_p = \frac{k_{2c}R_i^{1/2}K}{(k_{t22})^{1/2}}[M_1][M_2] \quad (23)$$

In case 1, the rate of copolymerization will be proportional to the concentration of the M_1(VCZ) monomer, being independent of the one of the M_2(FN or DEF) monomer, and the initial rate of copolymerization will increase linearly with the increase in the M_1 content in the monomer feed for a constant rate of initiation. In case 2, on the other hand, the rate equation is symmetrical with respect to $[M_1]$ and $[M_2]$, and the rate of copolymerization will show the maximum at the monomer feed composition of 1:1 (molar ratio) for a constant rate of initiation.[24] Since the overall rate features of the alternating radical copolymerization can be understood as the overlap of the independent rate features of the above two extreme cases, case 1 and case 2, the plots of the initial rates of copolymerization against the monomer feed molar ratios for a constant total monomer concentration can be depicted as in Figure 7. When the contribution of the monomer charge-transfer complex to the polymerization is very small and the reaction of the free monomers is predominant, the rate curve may be shown as the superposition of the rate curves (a_1) (case 2) and (b_1) (case 1), resulting in a curve (c), which almost resembles (b_1). When the contribution of the reaction of the monomer charge-transfer complex to the polymerization rate becomes appreciably large, the rate curve may be shown as the superposition of the rate curves (a_2) (case 2) and (b_2) (case 1), resulting in a curve (d), where the maximum point of the rate appears at a higher content of the M_1 monomer in the monomer feed, gradually

(24) Even if the unimolecular termination by the process of "burial" is partly involved in the VCZ-FN system which becomes heterogeneous as the polymerization proceeds, the same conclusion can be reached since it seems most probable that $m_2\cdot$ (FN end) can be a buried polymer radical by the same reason as in the bimolecular termination between $m_2\cdot$, and thus the stationary approximation is expressed as

$$R_i = k_{t22}[m_2\cdot]^2 + k_{t2}[m_2\cdot]$$

where k_{t2} is the rate constant for unimolecular termination. See M. Imoto and H. Takatsugu, *Macromol. Chem.*, 23, 119 (1957).

shifting toward the unity as the reaction of the monomer charge-transfer complex becomes predominant.[25]

The VCZ-DEF system, the rate curve of which resembles b_1 or c, is understood that in this system the contribution of the monomer charge-transfer complex to the polymerization is almost negligible, and that the reaction consists of almost only the free monomers. Indeed, it was found that the initial rate of copolymerization in this system was almost independent of the concentration of the M_2(DEF) monomer for a fixed concentration of the M_1(VCZ) monomer within experimental errors (Table III). By contrast, the VCZ-FN system, the rate curve of which resembles d, is understood that in this system reactions of both the monomer charge-transfer complex and the free monomers are operative in the propagation process of the polymerization.[26] The fact that the initial rates of copolymerization in the VCZ-FN system were five to twenty times faster than those in the VCZ-DEF system may be explained as due to much higher reactivity of the monomer charge-transfer complex[16] as compared with that of the free monomers.

Moreover, we can discuss the expected rate features of other special situations in the alternating radical copolymerization. Quite a similar treatment can be made in the case where the rate constant k_{21} is much greater than the rate constant k_{12}. When the rate constants k_{12} and k_{21}, and k_{1c} and k_{2c}, are of comparable order of magnitude with each other, and most termination occurs by the cross-reaction between $m_1\cdot$ and $m_2\cdot$, the overall rate equation will be reduced to eq 24. In this case the rate will

$$R_p = (2k_{21}k_{12}R_i/k_{t12})^{1/2}[M_1]^{1/2}[M_2]^{1/2} + (R_i/2k_{t12})^{1/2}\{(k_{21}/k_{12})^{1/2}k_{1c}K[M_1]^{3/2}[M_2]^{1/2} + (k_{12}/k_{21})^{1/2}k_{2c}K[M_1]^{1/2}[M_2]^{3/2}\} \quad (24)$$

maximize at the monomer feed molar ratio of 1:1 in both case 1 and case 2, respectively.[27]

Finally, it should be emphasized that all of the 1:1 alternating radical copolymerization can not be explained by the mechanism of homopolymerization of the monomer charge-transfer complex, which may be applied only to limited systems. In general, it is important to take account of the reactions of both the monomer charge-transfer complex and the free monomers. It is suggested that the degree of the contribution of each of them to the reaction, quantitative evaluation of which is left to a further study, varies greatly depending upon the reaction system. It can, therefore, be said that the regulation of 1:1 alternation in the polymer structure is not brought about solely by the participation of the monomer charge-transfer complex in polymerization, but rather stabilization of the transition state in the cross-propagation between a growing chain radical and a monomer including a monomer charge-transfer complex either by electrostatic interaction due to the different polarity or electron transfer is responsible for the regulation of the 1:1 alternating structure.

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(25) If it is assumed that the reactivity of the monomer charge-transfer complex is β times greater than that of the free monomer, *i.e.*, $k_{2c} = \beta k_{21}$, we obtain

$$R_p = (R_i/k_{t22})^{1/2}k_{21}\{2[M_1] + \beta K[M_1][M_2]\}$$
$$= (R_i/k_{t22})^{1/2}k_{21}A\{2x + \beta Kx(1 - x)\}$$

where $[M_1] + [M_2] = A$ (mol/l.); $[M_1]/([M_1] + [M_2]) = x$. Differentiating the above equation, we obtain

$$dR_p/dx = (R_i/k_{t22})^{1/2}k_{21}A\{2 + \beta K - 2\beta Kx\}$$

The maximum of R_p will appear at

$$x = (2 + \beta K)/2\beta K = (\tfrac{1}{2}) + 1/\beta K \geqq (\tfrac{1}{2})$$

(26) Although an attempt to evaluate the equilibrium constant K for the formation of the charge-transfer complex by means of nmr spectroscopy was not successful, the charge-transfer interaction may be stronger with the VCZ-FN system than the VCZ-DEF system in view of the greater electron-accepting strength of FN and the greater red shift in the electronic absorption spectra in the VCZ-FN system. It may also be possible that the VCZ-FN charge-transfer complex is much more activated in its reactivity than the VCZ-DEF complex.

(27) Substituting $(k_{21}/k_{12}) \approx (k_{12}/k_{21}) \approx 1$, and $k_{1c} \approx k_{2c}$, R_p in the case 2 is expressed as

$$R_p = (R_i/2k_{t12})^{1/2}k_{1c}K[M_1]^{1/2}[M_2]^{1/2}\{[M_1] + [M_2]\}$$

where

$$[M_1] + [M_2] = \text{const}$$

A ^{13}C Nuclear Magnetic Resonance Study of Alkane Motion

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ABSTRACT: Carbon-13 spin-lattice relaxation times (T_1) have been measured for resolved carbons in neat n-alkanes (n = 7, 10, 13, 15, 18, 20) and 2-methylnonadecane, and effective correlation times (τ_{eff}) have been calculated from the T_1 values. A self-consistent analysis of the τ_{eff} values is provided using a model which considers alkane carbon motion in terms of contributions from overall and internal rotations. This analysis yields values for the barriers to methyl rotation in the linear (2.6 kcal/mol) and branched (2.9 kcal/mol) alkanes that are in approximate agreement with previously reported values. One also obtains information on the effects of chain ends and branches on internal motion and an estimate of the number of carbons involved in segmental motion of long alkanes.

The measurement of nuclear spin-lattice relaxation times (T_1) provides information on the molecular dynamics of polymers.[2,3] The carbon-13 nucleus is particularly suited for such studies since the wide range of chemical shifts and the absence of spin-spin splittings, upon proton irradiation, normally enables T_1 values to be measured for many of the chemically distinct carbons of a polymer chain. The determination of ^{13}C T_1 values for individual main-chain and side-chain carbons makes it possible to probe directly segmental motion of the polymer backbone

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(2) (a) D. W. McCall, *Accounts Chem. Res.*, 4, 223 (1971). (b) J. Schaefer and D. F. S. Natusch, *Macromolecules*, 5, 416 (1972).

(3) J. Schaefer, *Macromolecules*, 5, 427 (1972).