

Alternating Copolymerization: A Recent Development in Radical Copolymerization

by

K. FUJIMORI AND N. A. WICKRAMASINGHE (formerly Mohottala)
*Department of Physical and Inorganic Chemistry,
University of New England, Australia.*

1. Introduction

In radical copolymerization, attention has long been drawn to the fact that individually unhomopolymerizable monomers such as stilbene and maleic anhydride can be copolymerized to form a copolymer of strictly 1 : 1 composition of the monomer unit. The copolymer was considered to be an alternating copolymer of -ABABAB- type of arrangement of comonomer units. The large steric hindrances in monomers were thought to be overcome by the strong polar interaction between the monomers.

Generally there have been three types of explanations proposed to the alternating copolymerization.

(1) The electrostatic interaction between oppositely polarized monomers and radicals decrease the activation energy of the cross-propagation step resulting in an alternating chain propagation.¹

(2) Charge transfer interactions occur between the monomers and the propagating radical ends of opposite polarities at the transition state to promote the alternating chain propagation.²

(3) The 1 : 1 charge transfer (CT) complexes formed between the oppositely polarized monomers are homopolymerized to give 1 : 1 alternating copolymers.³

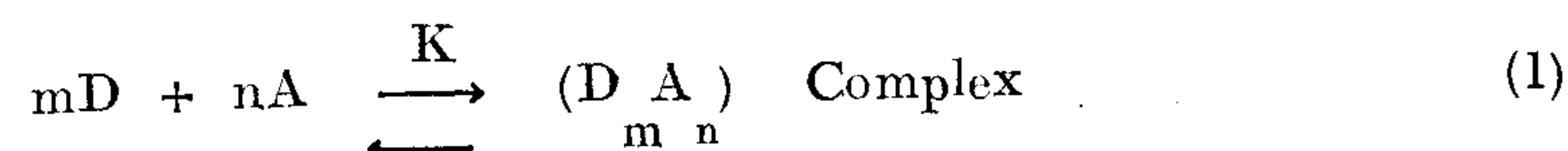
Recently, the realization that these polar monomers form CT complex has facilitated the understanding of the mechanism of alternating copolymerization. Such monomers as p-dioxene,⁴ 2-chloroethyl vinyl ether,⁵ ethyl vinyl ether,⁶ dihydropyran,⁶ which do not homopolymerize with radicals are now known to copolymerize easily with maleic anhydride, which has a strongly positively polarized C=C double bond (Alfrey-Price $e = 2.25$ and $Q = 0.23^7$). According to the mechanism, which is the most likely mechanism as will be seen below, it can be considered that the greater the donor and acceptor properties in forming CT complex, the larger the alternating tendency in the copolymerization. One of the measures of polarity of the monomers is the Alfrey-Price e -values,⁸ which are related to the electronic densities in the C=C double bonds. A monomer with a large positive e -value and a monomer with a large negative e -value would form a charge transfer molecular complex that leads to an alternating copolymer when polymerized radically.

2. Existence of charge transfer complex

2.1 Charge transfer complex between donor and acceptor monomers

In many cases of alternating copolymerization between oppositely polarized monomers, development of colour is observed when the monomers are mixed. In the ultra-violet region, a new peak of absorption appears on the shoulder of absorption peak of one of the monomers, indicating the formation of a CT complex between the monomers, in which an electron or a charge could transfer from a donor molecule to an acceptor molecule.

A complexation between a donor (D) and an acceptor (A) is generally expressed as :



$$K = \frac{[C]}{[D]^m [A]^n} = \frac{[C]}{\{ [D]_0 - m[C] \}^m \{ [A]_0 - n[C] \}^n} \quad (2)$$

where, [C] is the concentration of the complex, $[D]_0$ and $[A]_0$ are the initial concentrations of the donor and acceptor, respectively. K is the equilibrium constant of the complexation.

The stoichiometry of the complex (m and n in Eqn (1)) can be determined by applying the Job's continuous variation method to the UV absorption by the complex. Thus when the absorption due to the complex is plotted against the mole fraction of the component as shown in Fig. 1, the position of the maximum absorption shows the stoichiometry of the complexation. The position of the maximum is independent of the wavelength.

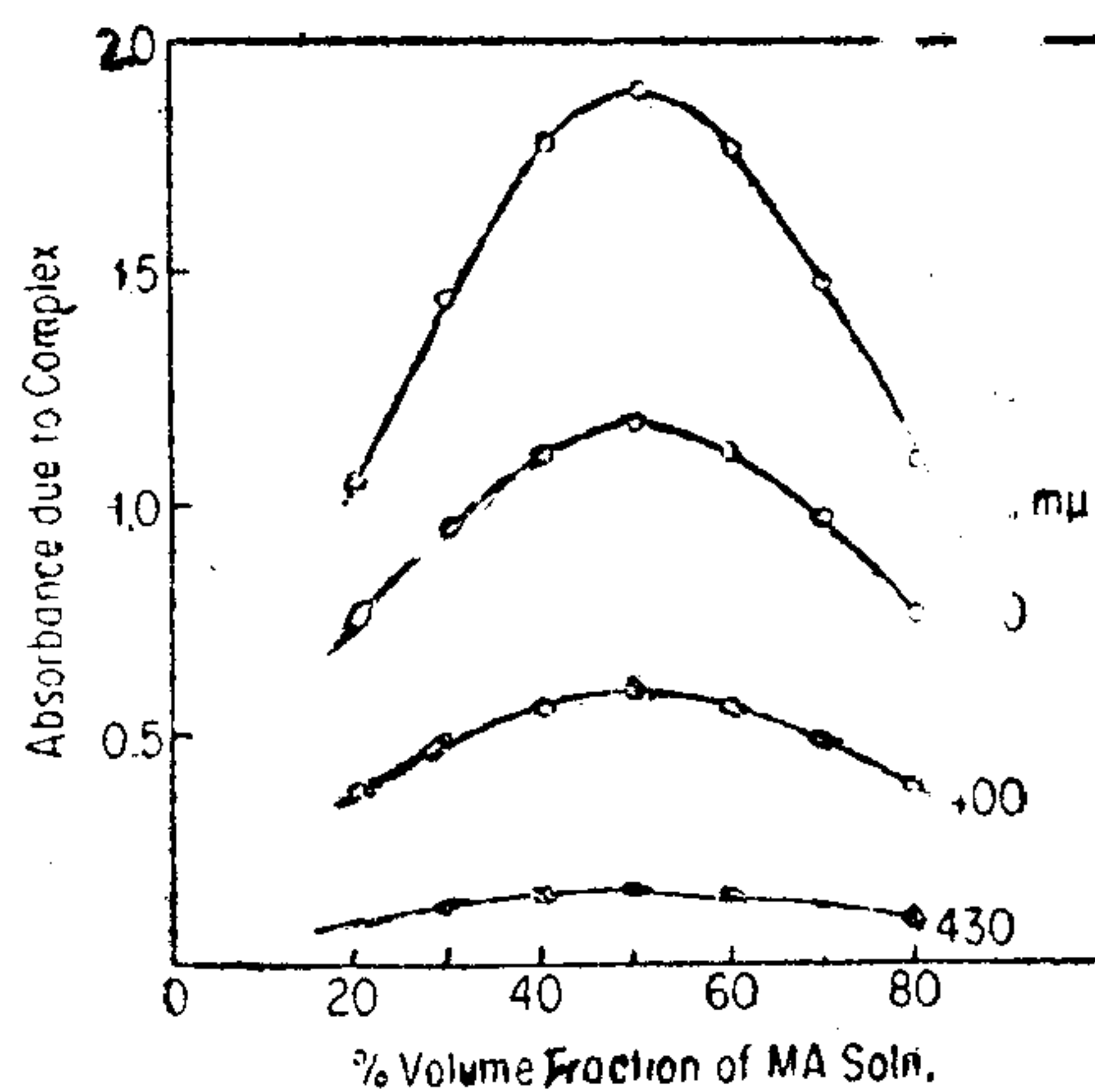
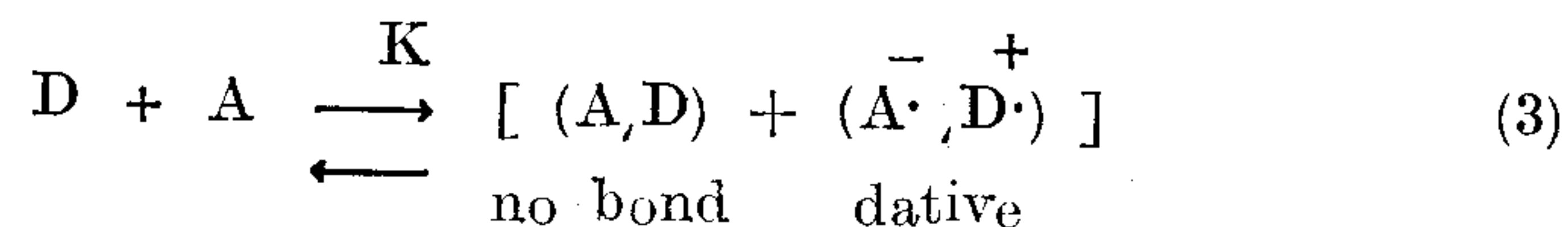


Fig. 1. Analysis by the continuous variation method
Solvent: chloroform, concentration of PD solution: 0.5045 mole/l, concentration of MA solution: 0.5082 mole/l.

In all cases, the stoichiometry of complexation has been reported to be 1 : 1. For example, the donor-acceptor pairs of p-dioxene-maleic anhydride,¹⁰ styrene-maleic anhydride¹¹, 1-olefins-sulfur dioxide,¹² and substituted styrene-maleic anhydride¹³ all form 1 : 1 CT complexes.

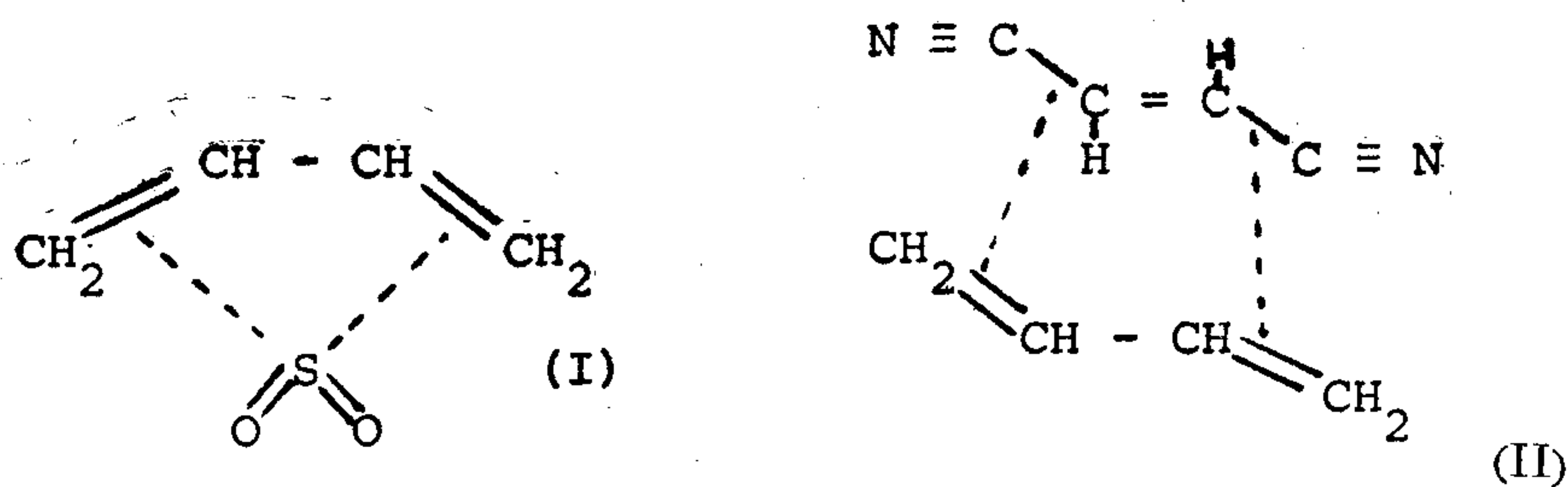
A CT complex is in equilibrium with the free components. The CT complex exists in resonance between the no-bond state and the charge transferred dative state. Thus the wave function of the complex (ψ_{CT}) can be expressed as a linear combination of wave functions of the no-bond state ($\psi(A,D)$) and the dative state ($\psi(A^{\cdot-}, D^{\cdot+})$) as in Eqn. (4). The geometry of the complex is thought to be the one which



$$\psi_{CT} = a\psi(A,D) + b\psi(A^{\cdot-}, D^{\cdot+}) \quad (4)$$

accomplishes a maximum overlapping of the π -orbitals, with the planar vinyl groups of the donor and the acceptor monomers packed parallel each other.

It is interesting to note that the alternating copolymerization of 1,4-butadiene, predominantly cis-1,4-structure of the butadiene unit appears in the copolymer with sulfur dioxide or with maleic anhydride as seen in Table 1. A cis type of CT complex (I) is proposed. On the other hand, the copolymerization with fumaronitrile,



in which a trans type of CT complex (II) is possible, the butadiene units in the resultant copolymer are found to be predominantly trans-1,4-structure.¹⁵

TABLE 1
The Microstructure of Butadiene Copolymers¹⁵

<u>Comonomer</u>	<u>cis-1,4%</u>	<u>trans-1,4%</u>	<u>1,2-%</u>
None	16.4	61.7	21.9
Sulfur dioxide	61.6	38.4	0
Maleic anhydride	73.7	12.6	13.7
Fumaronitrile	13.4	77.1	9.5

2-2 Determination of the equilibrium constant of complexation

The equilibrium constant (K) of CT complexation can be determined by both UV and NMR spectroscopy. Ketelaar et al¹⁶ have derived a relation between the absorptivity of the complex in the UV and the concentration of the components in the case of 1 : 1 complexation (Eqn. (5))

$$\frac{1}{(\epsilon_A - \epsilon_a)} = \frac{1}{K[D]} \left(\frac{\epsilon_c - \epsilon_a}{\epsilon_c} \right) + \frac{1}{(\epsilon_c - \epsilon_a)} \quad (5)$$

where, [D] is the concentration of the donor. ϵ_A is related to the measured optical density, d_A , and to the total molar concentration of both free and complexed acceptor [A] by the expression $d_A = \log_{10} I_0/I = \epsilon_A[A]l$. ϵ_c and ϵ_a represent the extinction coefficients of the complex and uncomplexed acceptor, respectively. Thus the plot of $1/(\epsilon_A - \epsilon_a)$ versus $1/[D]$ should give a straight line from which K and ϵ_c can be determined.

When a very small concentration of an acceptor and a large excess of donor are used, it can be assumed that all the acceptor is complexed. Under this condition, K can be determined through either the equation by Bensi and Hildebrand (Eqn. (6))¹⁷ or the equation by Scott (Eqn. (7))¹⁸.

$$[A]l/d_c = 1/\epsilon_c K[D] + 1/\epsilon_c \quad (6)$$

$$[A][D]l/d_c = [D]/\epsilon_c + 1/\epsilon_c K \quad (7)$$

where, $[A] \ll (D)$, d_c is the absorbance due to the complex only, i.e., $d_c = d(\text{overall}) - d(\text{donor})$ and l is the path length in cm. The plot of $[A]l/d_c$ or $[A][D]l/d_c$ against $1/[D]$ or $[D]$, respectively, gives a straight line from which K and ϵ_c can be determined. By using both equations simultaneously, errors in $1/\epsilon_c$ from Eqn. (6) and of $1/K\epsilon_c$ in Eqn. (7) can be minimized.

The NMR method is more accurate and easier to use in the case of weak complexes such as the one between vinyl ether and maleic anhydride, the UV absorption maximum is often near that of one of the components when the donor is always in large excess compared to the acceptor. The relation between the chemical shift of the acceptor, and the donor concentration [D], when the concentration of the acceptor is fixed, has been derived by Hanna and Ashbough¹⁹ (Eqn. (8)).

$$1/\Delta_{\text{obs}}^A = 1/K \Delta_c^A [D] + 1/\Delta_c^A \quad (8)$$

where, $\Delta_{\text{obs}}^A = \delta_{\text{obs}}^A - \delta_0^A$, is the difference between the chemical shift of the acceptor proton in complexing media (δ_{obs}^A) and that of the acceptor in uncomplexed form (δ_0^A), and $\Delta_c^A = \delta_c^A - \delta_0^A$ is the difference in the acceptor proton in pure complex (δ_c^A) and free acceptor. The straight line obtained by plotting $1/\Delta_{\text{obs}}^A$ against $1/[D]$ gives the value of K and Δ_c^A from which δ_c^A can be calculated.

TABLE 3
THERMODYNAMIC CONSTANTS^{a)} OF COMPLEXATION IN
VARIOUS SOLVENTS

Solvents	DME-MA ^{b)}			CEVE-MA ^{c)}			PD-MA ^{d)}		
	ΔG Kcal/ mol	$-\Delta H$ Kcal/ mol	$-\Delta S$ eu	ΔG Kcal/ mol	$-\Delta H$ Kcal/ mol	$-\Delta S$ eu	ΔG Kcal/ mol	$-\Delta H$ Kcal/ mol	$-\Delta S$ eu
Benzene	0.72	1.91	8.9	1.37	1.55	9.8	1.58	1.11	9.0
Toluene	1.07	1.74	9.4				1.91	0.92	9.5
Chlorobenzene	1.03	2.04	10.3				1.77		
Chloroform	1.13	0.99	7.1	1.32	0.86	7.3	1.73	0.65	8.0
Acetone	1.42	0.90	7.8				1.81		

(a) At 25°C, calculated from $\Delta G = RT \ln K$ and $\Delta G = \Delta H - T \Delta S$ using K and $\ln K$ v.s. $1/T$.

(b) CT complex of 1,2-dimethoxy ethylene and maleic anhydride

(c) CT complex of 2-chloroethyl vinyl ether and maleic anhydride

(d) CT complex of p-dioxene and maleic anhydride

2-3 Solvent effects on equilibrium constant

It has been found that the magnitude of the equilibrium constant (K) decreases with increasing polarity of the solvent. Table 2 shows that these complexes are not sufficiently ionic to initiate ionic polymerization, the contribution of the dative state being not very significant. But in the case of the complex of N-vinyl carbazole with p-chloranil, the K value is very large (3 and 6 in toluene and in acetonitrile, respectively), it increases with the solvent polarity, and the complex initiates cationic polymerization, indicating that the contribution of a dative structure may be significant.²⁰

The data in Table 3 shows the different influence of aromatic and non-aromatic solvents. Aromatic solvents act as π -donors, on the other hand, non-aromatic solvents act as n -donors, due to the lone pairs of oxygen or nitrogen, and chloroform as σ -acceptor due to the σ bonds between the carbon atom and chlorine atoms. Therefore, the remarkable difference in ΔH and ΔS may depend upon whether they are π -donors or not⁵.

2-4 Relation between the overall rate of alternating copolymerization and the equilibrium constant of complexation

From Table 4⁵⁾ it is seen that the overall rate of the alternating copolymerization of dimethoxy ethylene and maleic anhydride is more rapid in a solvent in which the K value is larger, i.e. more complex is present. On the other hand, it is well known that generally the rate of radical polymerization is not affected by the solvent polarity.

TABLE 4
Comparison of the Rate of Copolymerization and K for the System
of 1,2-dimethoxyethylene-maleic anhydride^{a)}

<i>Time in min.</i>	Conversion in %		
	<i>Toluene</i>	<i>Benzene</i>	<i>m-Xylene</i>
22	2.03	2.41	2.32
75	6.55	6.98	8.19
120	11.2	10.3	19.4
180	11.7	18.0	15.2
mean rate ^b	0.080	0.093	0.110
K^c	0.16	0.29	0.73

(a) 30°C, feeds [DME] = 0.397 g, (MA) = 0.441 g, solvent 2.5 cm³

(b) in percent per minute, (c) values at 25°C.

Alternating Copolymerization: A Recent Development in Radical Copolymerization

When a CT complex is a weak one predominated by the no-bond state, the equilibrium constants of the complexation generally decreases with the increase of solvent polarity, because in polar solvents free monomers are better stabilized than the complex of the monomers. The overall rate of the alternating copolymerization of dihydropyran and maleic anhydride is found to decrease with increasing dielectric constant of the solvent as shown in Fig. 2⁶. The importance of the CT complex is apparent both in Table 4 and Fig. 2.

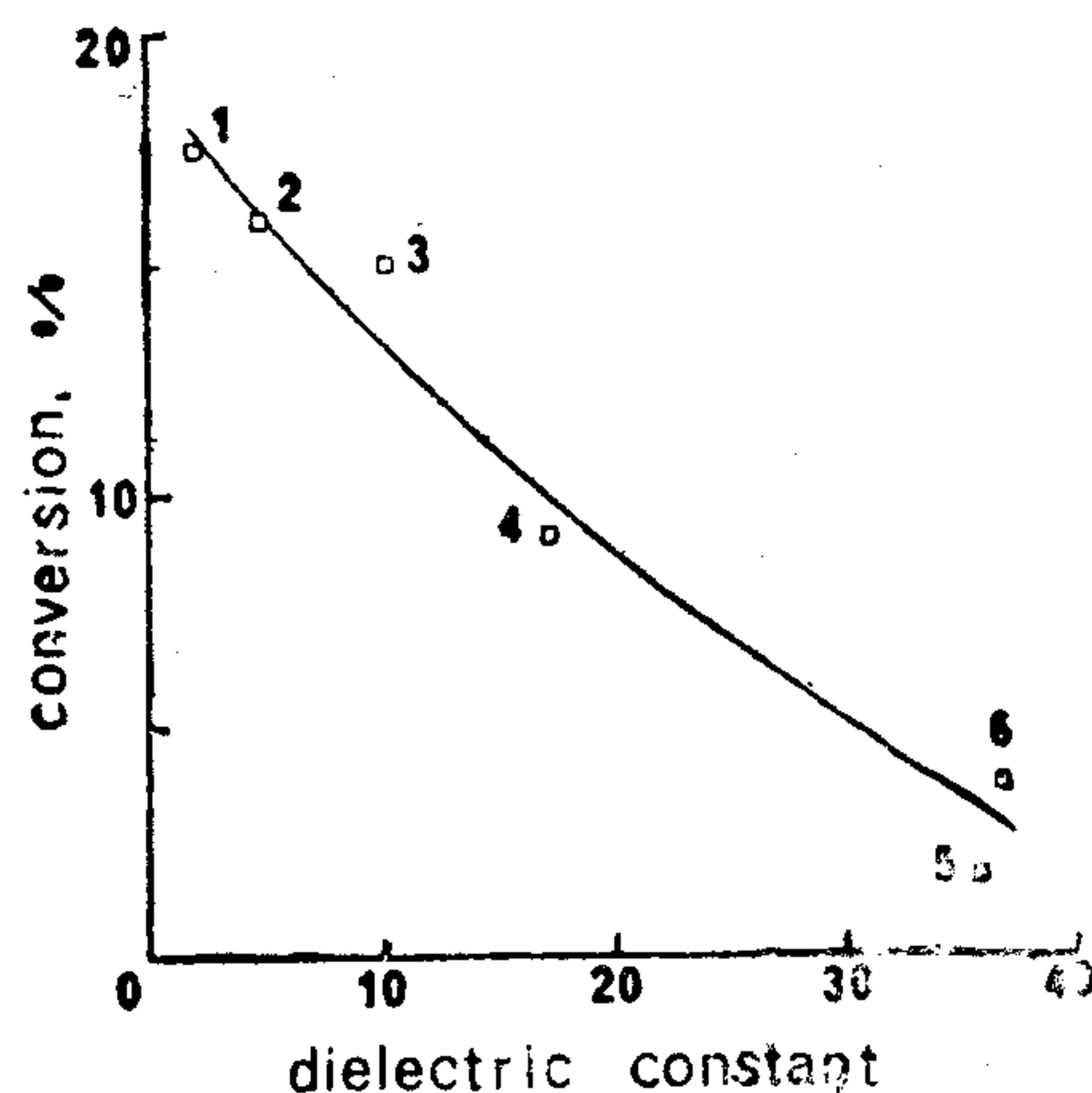


FIG. 2. Effect of the polarity of solvents on the conversion of equimolar copolymerization of DHP with MA after 10 hr at 60°C [DHP + MA] = 1.86 mole/liter, [BPO] = 1.82×10^{-2} mole/liter, (1) Dioxane, (2) chloroform, (3) 1,2-dichloroethane, (4) acetophenone, (5) nitromethane and (6) dimethylformamide.

3. Proof of the copolymerization mechanism by terpolymerization

3-1 Application of random terpolymerization mechanism by Alfrey and Goldfinger

If a terpolymerization is regarded as the propagation of three kinds of growing chain ends $-m_1$, $-m_2$, and $-m_3$ in a random fashion, there are nine different elementary chain propagation reactions. The initial terpolymer composition, $m_1/m_2/m_3$, derived by Alfrey and Goldfinger is in Eqn. (9)²¹

$$\left. \begin{aligned} \frac{m_1}{m_2} &= \frac{r_2 R_3 M_1 M_2 + r_3 M_1 (r_2 M_1 + R_2 M_3)}{r_1 r_3 M_1 M_2 + R_3 M_2 (r_1 M_2 + R_1 M_3)} \cdot \frac{M_1 + r_1 M_2 + R_1 M_3}{M_3 + r_2 M_1 + R_2 M_3} \\ \frac{m_1}{m_3} &= \frac{r_2 R_3 M_1 M_2 + r_3 M_1 (r_2 M_1 + R_2 M_3)}{R_1 r_2 M_1 M_3 + R_2 M_3 (r_1 M_2 + R_1 M_3)} \cdot \frac{M_1 + r_1 M_2 + R_1 M_3}{M_3 + r_3 M_1 + R_3 M_1} \end{aligned} \right\} (9)$$

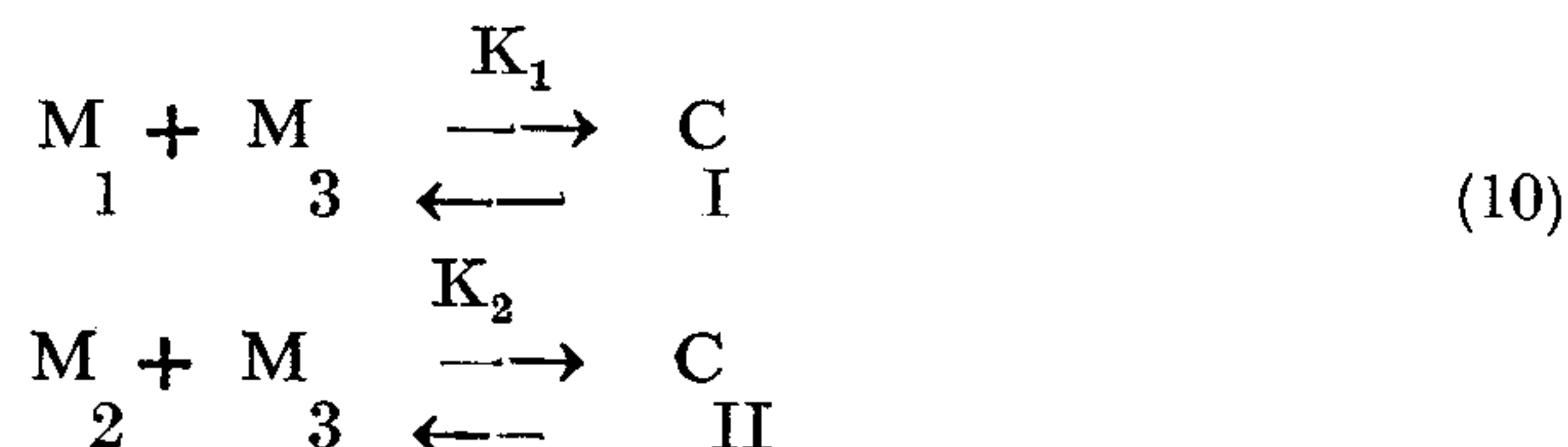
where, $r_1 = k_{12}/k_{11}$, $r_2 = k_{21}/k_{22}$, $r_3 = k_{31}/k_{33}$,

$R_1 = k_{13}/k_{11}$, $R_2 = k_{23}/k_{22}$ and $R_3 = k_{32}/k_{33}$ are the ratios of the

are the ratios of the rate constants of the propagation elementary reactions. The values of r_1 , r_2 , and r_3 can be obtained from individual binary copolymerizations and the constants R_1 , R_2 and R_3 are calculated by using the experimental results of the terpolymerization. In the terpolymerization where two of the monomers can undergo alternating copolymerizations, such as the systems of acrylonitrile-p-dioxene-maleic anhydride^{22,10}, β -chloroethylacrylate-p-dioxene-maleic anhydride²³, β -chloroethylacrylate-dodecyl vinyl ether-fumaronitrile²⁴, and anethol-maleic anhydride-fumaronitrile²⁵, it has been shown that the values of R_1 , R_2 and R_3 are not constant but change significantly with the feed composition when the Alfrey-Goldfinger equation is applied. This indicates that the propagation reactions of the monomers which form CT complexes should not be regarded as random processes.

3-2 Copolymerization of two kinds of CT complexes

According to the complex mechanism, a CT complex is expected to behave as a monomer. Some terpolymerization systems can be regarded as the systems of two kinds of complexes (C_I and C_{II}) when two of the monomers act as the acceptors for the third monomer, which acts as the donor, or when two of the monomers act as the donors for the third monomer which is the acceptor. The two equilibria are expressed as follows:



where, K_1 and K_2 are the equilibrium constants. The concentrations of the complexes are, therefore, $[C_I] = K_1 [M_1][M_3]$ and $[C_{II}] = K_2 [M_2][M_3]$. If the terpolymerization is treated as a binary copolymerization²⁶) of C_I and C_{II} the composition equation for the terpolymerization is expressed as a function of the equilibrium constants.

$$\begin{aligned} \frac{-d[M_1]/dt}{-d[M_2]/dt} &= \frac{m_1}{m_2} = \frac{[C_I]}{[C_{II}]} \left\{ \frac{r_1[C_I] + [C_{II}]}{[C_I] + r_2[C_{II}]} \right. \\ &= \frac{[M_1]}{[M_2]} \left\{ \frac{r_1 (K_1/K_2) [M_2] + [M_3]}{[M_2] + r_2 (K_2/K_1) [M_3]} \right. \end{aligned} \quad (11)$$

From the terpolymerization results, $r_1 (K_1/K_2)$ and $r_2(K_2/K_1)$ can be determined from Eqn. (11), which correspond to the apparent monomer reactivity ratios of the complexes C_I and C_{II} , respectively.

The binary system of chloroethyl vinyl ether (CEVE) and maleic anhydride, and that of CEVE and fumaronitrile individually give alternating copolymers. The terpolymerization system of CEVE, maleic anhydride and fumaronitrile is found to give terpolymers in which the mole fraction of CEVE unit is always 0.50. The apparent monomer reactivity ratio of the complexes of CEVE and fumaronitrile (C_I), and CEVE and maleic anhydride (C_{II}) are found to be :

$$r_1(K_1/K_2) = 2.5 \pm 0.5 \text{ for } C_I$$

$$r_2(K_2/K_1) = 0.2 \pm 0.2 \text{ for } C_{II}$$

The results are compared in Fig. 3 between the treatment based on the complex mechanism by Eqn. (11) (solid line) and the free propagation treatment by Eqn. (9) (dotted line)²⁷. Notice that the solid line covers more experimental results.

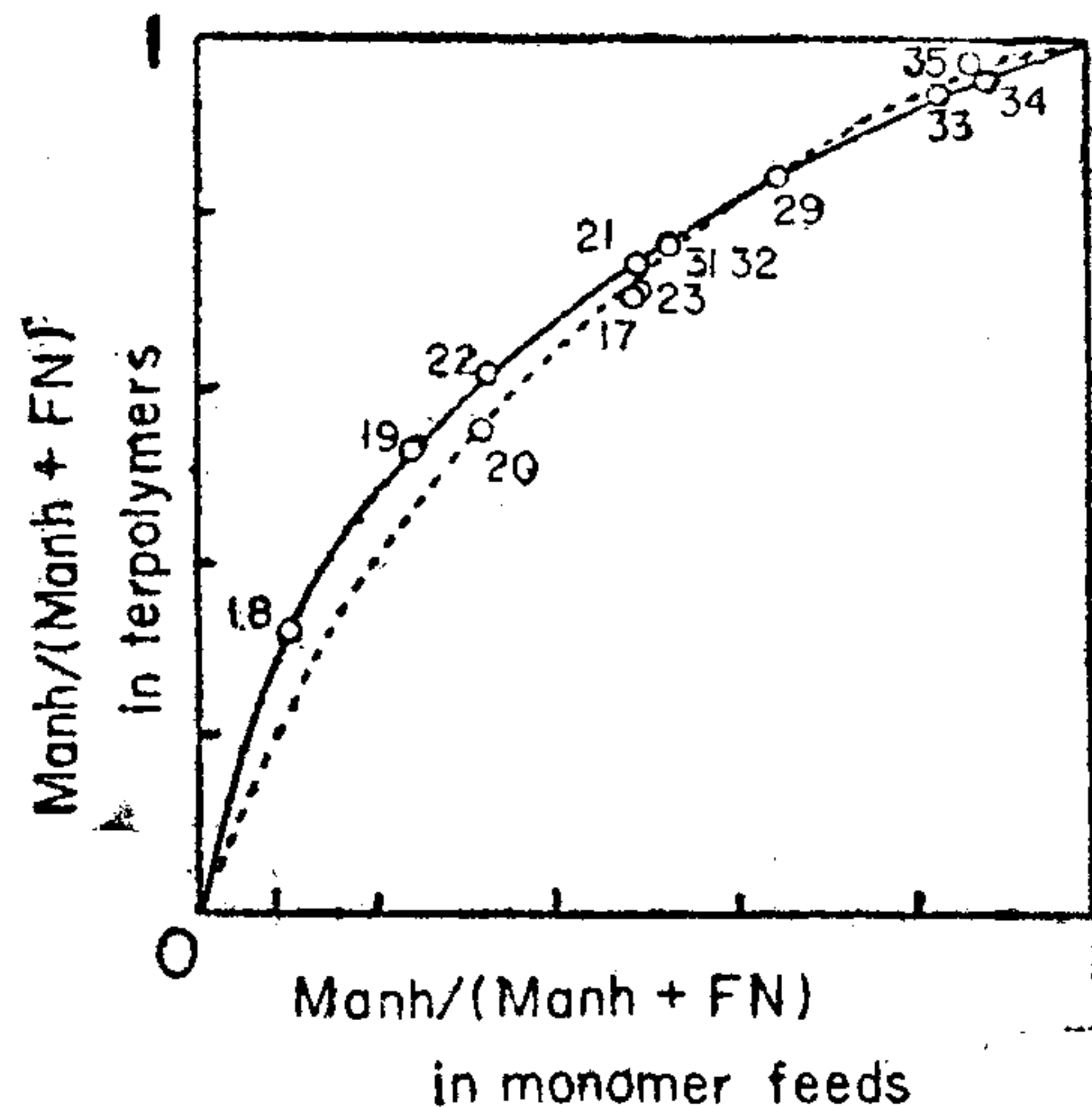


Fig. 3. The composition ratio of feed and terpolymer with regard to Manh and FN in the case of the terpolymerization of 2-chloroethyl vinyl ether/maleic anhydride/fumaronitrile (CEVE/Manh/FN) system.

The terpolymerization of CEVE, p-dioxene and maleic anhydride, in which there are two donors and one acceptor, has been successfully treated by Eqn. (11)²⁷.

3.3 Copolymerization of a CT complex and a non-complexing third monomer

For a terpolymerization system, in which two of the monomers form a CT complex between them but the third monomer is non-complexing, it can be regarded that, according to the complex mechanism, that the complex and the third monomer copolymerize randomly. Thus, Eqn. (12) is obtained by applying the Mayo-Lewis copolymer composition equation²⁶, where the concentration of the complex is expressed as $[C] = K[D][A]$.

$$\frac{-d[C]/dt}{-d[M_3]/dt} = \frac{d[A] \text{ or } d[D]}{d[M_3]} = \frac{[A][D]}{[M_3]} \left\{ \frac{r_1 K[A][D] + [M_3]}{[A][D] + (r_2/K)[M_3]} \right\} \quad (12)$$

The apparent monomer reactivity ratios of the complex and the third monomer r_1K and r_2/K , respectively, can be determined from the terpolymerization,

The system of anethol, maleic anhydride and acrylonitrile is an example that falls in this category, acrylonitrile being uncomplexing monomer (M_3). The apparent monomer reactivity ratios are determined to be r_1K (complex) = 45 ± 2.9 and r_2/K (acrylonitrile) = 0.0079 ± 0.0024 . The copolymer composition curve for this terpolymerization is shown in Fig. 4²⁵.

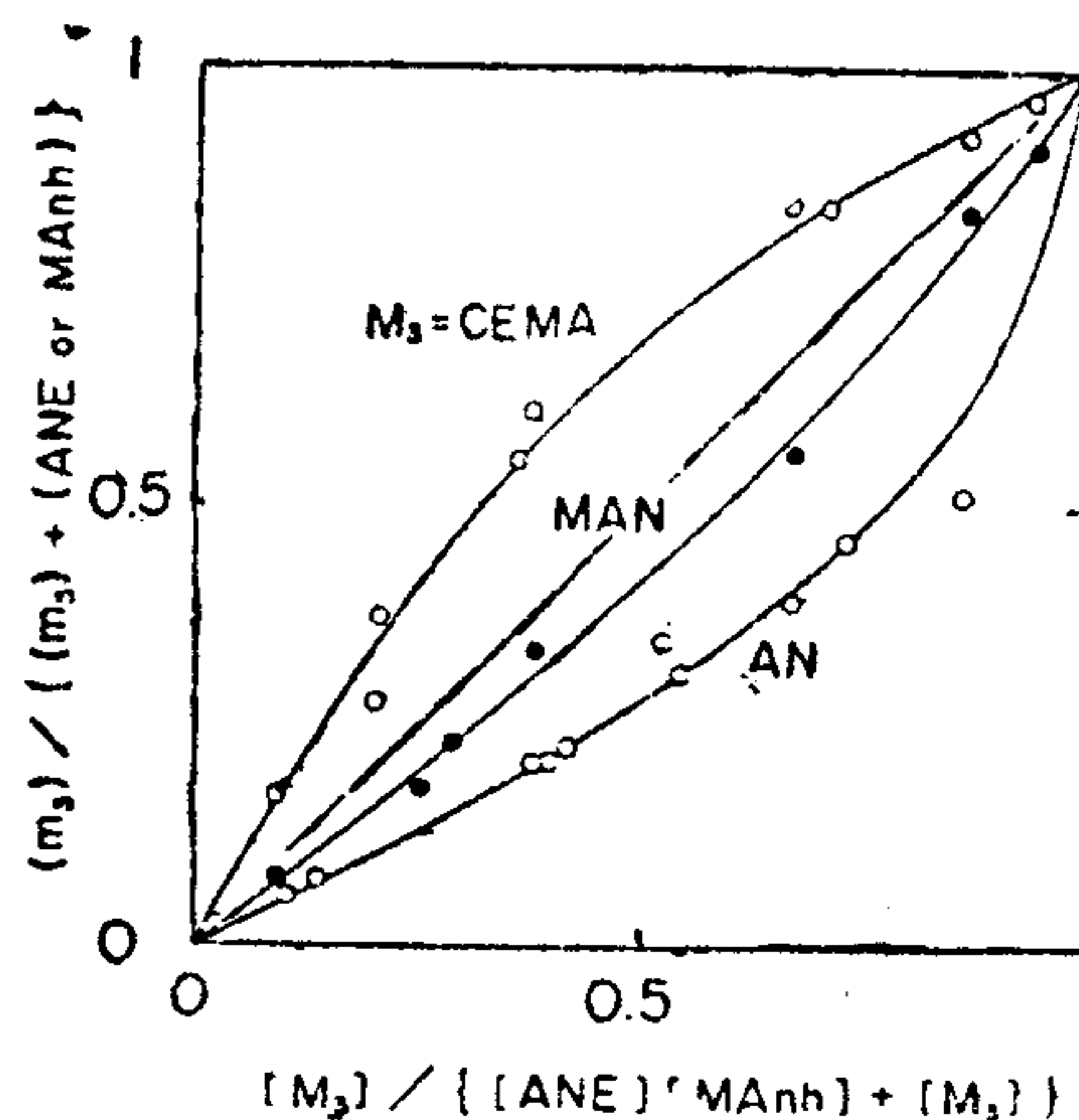


Figure 4. Copolymer composition diagram of ANE-MANh- M_3 systems as binary copolymerizations between ANE-MANh Complex and M_3

If the equilibrium constants of complexation are known, the true "monomer" reactivity ratios of the complexes can be calculated. In Table 5 some of the true monomer reactivity ratios of CT complexes determined through the terpolymerization technique are shown.

TABLE 5
Monomer Reactivity Ratios in Benzene at 60°C

System ^{a)}	First Component	Second Component	Apparent monomer reactivity ratios	r_1	r_2	ref.
CEVE-PD-MA	(CEVE-MA)	(PD-MA)	$r_1(K_1/K_2) = 2.05$ $r_2(K_2/K_1) = 0.34$	1.52	0.46	28)
CEVE-PD-AN	(CEVE-MA)	AN	$r_1K_1 = 0.36$ $r_2/K_1 = 1.25$	4.8	0.093	29)
PD-MA-AN	(PD-MA)	AN	$r_1K_1 = 0.28$ $r_2/K_1 = 3.6$	5.0	0.189	4)

a) CEVE = chloroethyl vinyl ether, PD = p-dioxene, MA = maleic anhydride, and AN = acrylonitrile

Alternating Copolymerization: A Recent Development in Radical Copolymerization

It is interesting to compare the relative reactivities of the CT complexes of CEVE and maleic anhydride, and of p-dioxene and maleic anhydride toward acrylonitrile radical. In Table 6, the relative reactivity of the complexes and the component monomers are compared. The ratio of the rate constant of acrylonitrile radical attacking a comonomer (k_{AN-M_1}) to that of acrylonitrile radical attacking acrylonitrile monomer (k_{AN-AN}) is the reciprocal value of r_2 . It is seen that the reactivity of the CT complex is much larger than that of the component individual monomers. It is considered that the relatively small concentration of the CT complex in the polymerization system is more than compensated by the enhanced reactivity of the CT complex toward a radical.

TABLE 6

Relative Reactivity of Complexes and the Component Monomers
Toward Acrylonitrile Radical^{a)}

Component 1 (M_1) ^{b)}	r_2	k_{AN-M_1}/k_{AN-AN}
C(CEVE-MA) ..	0.092	11
C(PD-MA) ..	0.183	6
CEVE monomer ..	1.0	1.0
PD monomer ..	5.9	0.17
MA monomer ..	6.0	0.17

(a) The component 2(M_2) is acrylonitrile

(b) CEVE = chloroethyl vinyl ether, MA = maleic anhydride and
PD = p-dioxene

3.4 Classification of charge-transfer polymerization systems

The magnitude of the K values may be used to classify the behaviour of CT complexes in alternating copolymerization. Some donor-acceptor pairs such as p-dioxene-maleic anhydride pair, or styrene-maleic anhydride pair, alternating copolymers are tained without initiators. The dative state of the complex is thought responsive to do auto-initiation. The K values of these systems fall approximately between 10^{-2} and 1. The systems where K values are below this range can undergo alternating copolymerization with initiators. The alternating tendency decreases as the value of K becomes even smaller. As the determination of K values becomes impossible, the copolymerization becomes random.

For the systems that show large K values such as $K = 5$ or 6 , the complexes are considered to be largely in the dative state, which initiates ionic polymerization. Hence, alternating copolymerization is no longer possible. The classification is summarized in Table 7⁵.

TABLE 7
Classification of Charge-Transfer Polymerizations

K	Class	Examples (K, solvent, temp.)	Behaviour
↑	A		No alternating copolymerization.
0.01	B	cyclohexene- SO_2 (0.053, n-heptane, 25°) ¹² PD-MA (0.055, CCl_4 , 25°) cis-2-butene- SO_2 (0.076, n-heptane, 25°) ¹² trans-2-butene- SO_2 (0.086, n-heptane, 25°) ¹²	Alternating copolymerization in the presence of initiator.
0.1	C	CEVE-MA (0.10, CCl_4 , 30°) DME-MA (0.15, CCl_4 , 25°) 1-methycyclopropene- SO_2	spontaneous alternating copolymerization near at room temperature. (The K values decrease with increasing solvent polarity).
1.0		N-vinylcarbazole-p-chloranil	(Spontaneous) ionic polymerization.
5.0	D	(3.2 & 6.6, toluene & acetonitrile) ²⁰ N-vinylcarbazole- SO_2 , X ₂ ³⁰	(The K value increases with increasing solvent polarity).
∞	E	4-vinylpyridine-p-chloranil (3:1 adduct)	Formation of separable, stable complexes which cannot initiate.

3-5 Solvent and Dilution

When a terpolymerization system of two complexing monomers and an uncomplexing third monomer is gradually diluted with solvent, the concentration of the complex decreases much faster than that of the uncomplexing monomer. Therefore, a dilution effect on the composition of the terpolymer is expected. Figs. 5 and 6¹⁰ show the solvent and dilution effects on chloroethyl vinyl ether-maleic anhydride-acrylonitrile (CEVE-MA-AN) system and

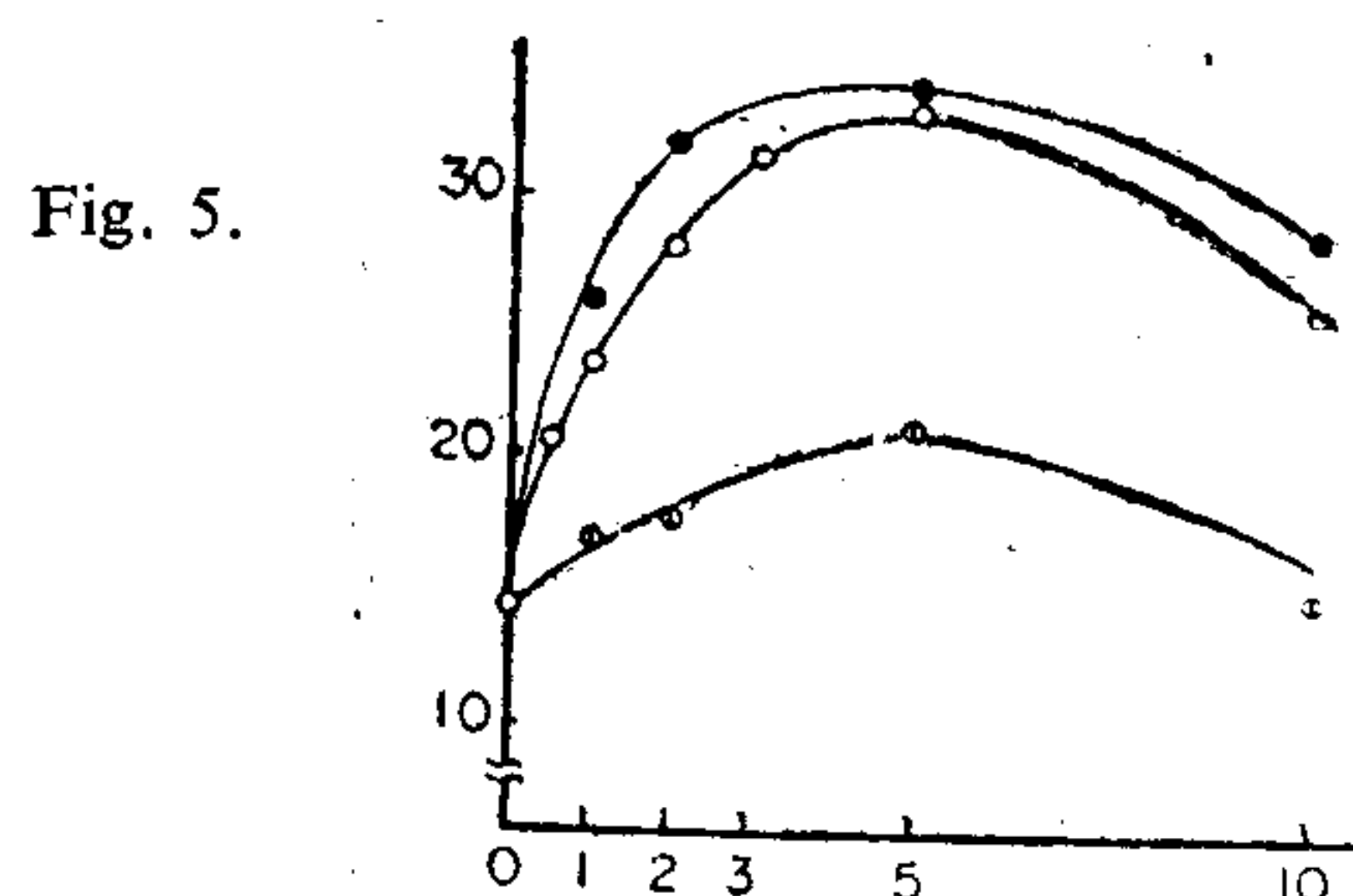


Fig. 5.

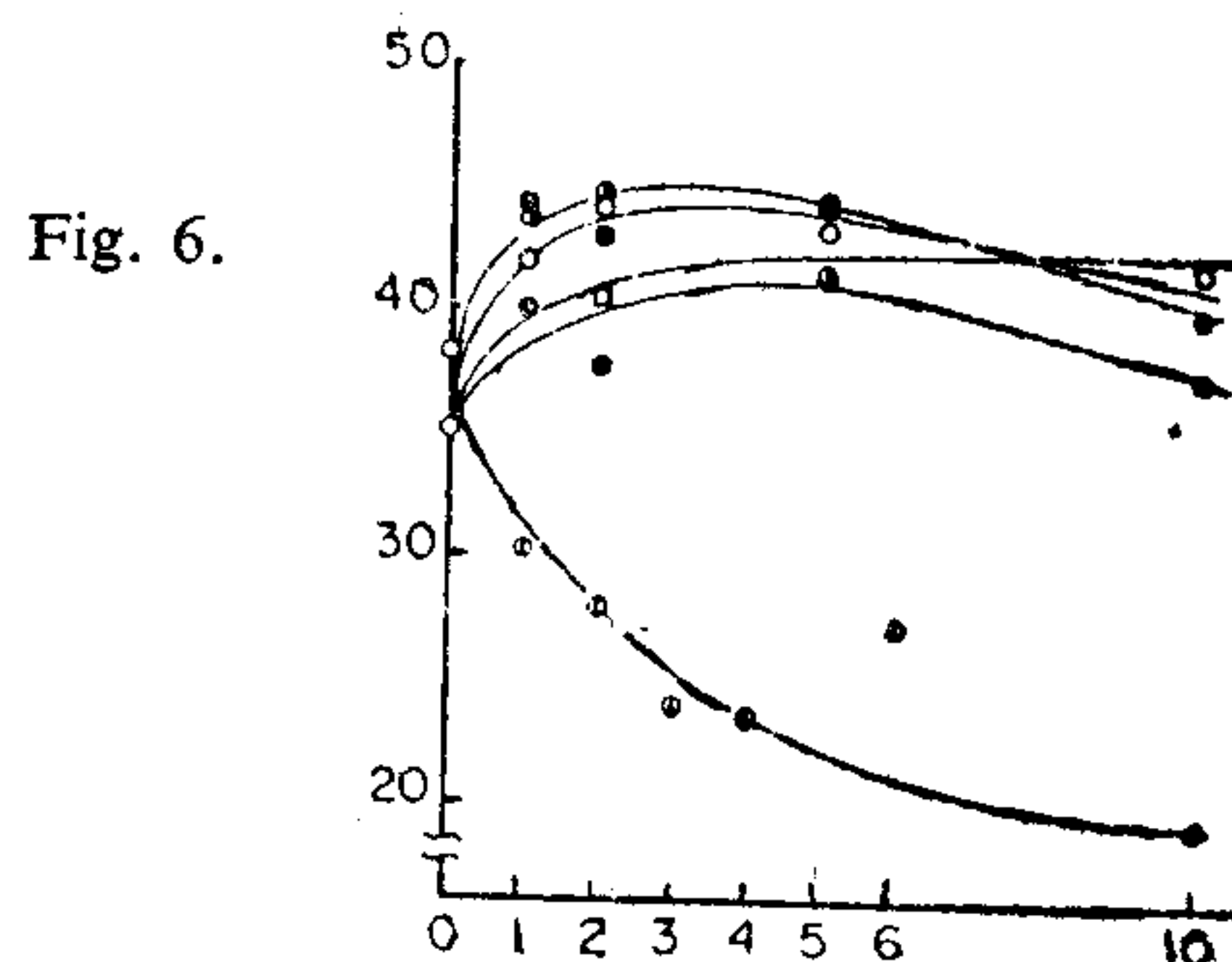


Fig. 6.

Fig. 5. Dependence of composition of terpolymers from same feed on amount and kind of solvent in CEVE-MAh-AN system. Abscissa, volume of solvent, in milliliters; ordinate AN content in terpolymer, in mole percentage; (○) Bz, (●) Tol, (○) CHCl_3 .

Fig. 6. Dependence of composition of terpolymers from same feed on amount and kind of solvents in PD-MAh-AN system. Abscissa, volume of solvent, in milliliters; ordinate, AN content in terpolymer, in weight percentage; (○) Bz, (●) Tol, (○) *m*-Xyl, (□) acetone, (●) CHCl_3 , (●) ClB.

p-dioxene-maleic anhydride-acrylonitrile (PD-MA-AN) system, acrylonitrile being the uncomplexing monomer. Except for the PD-MA-AN system polymerized in chloroform the increase of the acrylonitrile content in the terpolymer is consistent with the expected dilution effect on the concentrations. However, on further dilution, the acrylonitrile content begins decreasing. The first part could be explained by a dilution effect as shown in Eqn. (13) which is the Eqn. (12) expressed in terms of mole fractions.

$$\frac{d[\text{complex}]}{d[M_1]} = \frac{[X_2][X_3]}{[X_1]} \left\{ \frac{r_1 K [X_2][X_3][M] + [X_1]}{[X_3][X_2] + (r_2/K) [X_1](1/[M])} \right\} \quad (13)$$

where, x_i is the mole fraction of the i -th component and $[M]$ is the total monomer concentration. The dilution decreases the total monomer concentration (M), and the consequence will be the decrease of complex, hence the increase of the third monomer, in the resultant terpolymer according to the Eqn. (13).

The second part of the curves, in which the acrylonitrile content in the terpolymer decreases as the amount of solvent increases, is apparently due to the fact that the reactivity of the complex may be increased owing to the solvation on the complex. From the height of the maxima, the order of the reactivity of complexes is m -xylene \leq toluene \leq benzene \leq acetone \leq chlorobenzene \leq chloroform. This order disagrees with that of the dipole moments. However, the order of π -electron density in this series of aromatic solvents agrees with this change in reactivity of the complex⁵. Therefore it is proposed that when a π -electron rich solvent solvates on an electron-poor complex, the complex becomes more stable to a free radical attack. The Alfrey-Price Q and e values are determined for the CT complexes as in Table 8. As the e -values show, the

TABLE 8
Alfrey-Price Q and e Values for
the Complexes

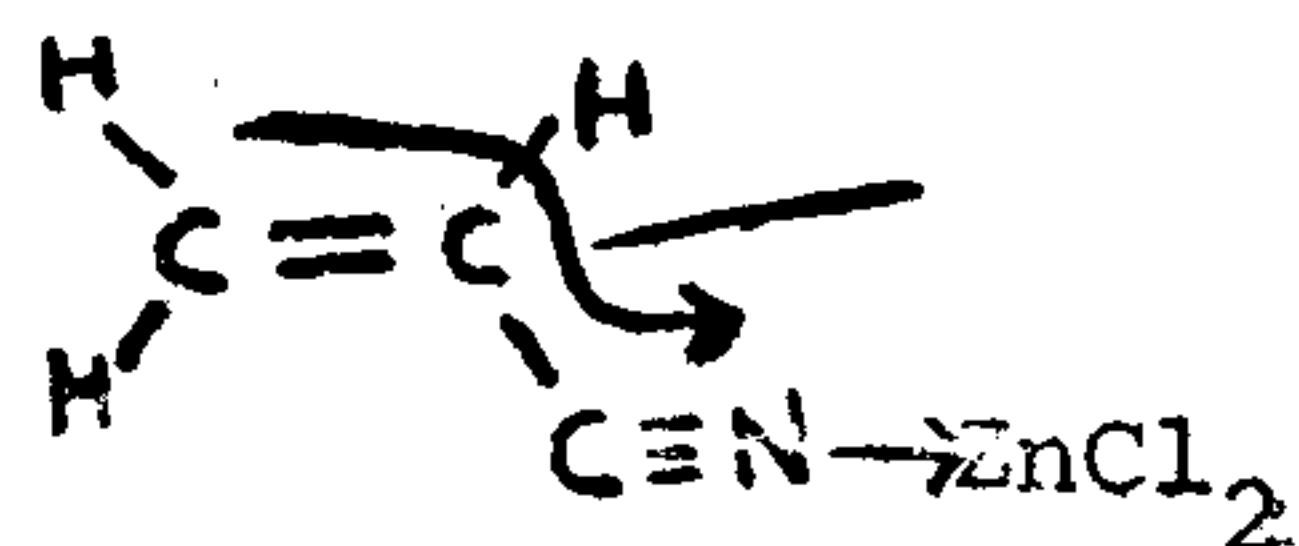
		<i>PD-MA complex</i>	<i>CEV. MA complex</i>	<i>acrylo- nitrile</i>
Q	..	2.4	2.1	0.60
e	..	0.98	0.1	1.20

electron positive PD-MA complex is stabilized better by the solvation of π -electron rich solvents but the acceptor property of chloroform may not stabilize the reaction site of the complex, and the reactivity of the complex remains large in chloroform.

4. Effect of Lewis acids in alternating copolymerization

Polar vinyl monomers containing pendent nitrile or carbonyl group such as acrylic monomers, copolymerize alternately with donor monomers in the presence of metal halides such as $ZnCl_2$ and $AlCl_3$. Such polymerizations

are characterized by increased rate of polymerization and generally high molecular weights^{31,34}. Imoto and Ohtsu^{33,35} have proposed that this may be due to the formation of a Lewis acid-base complex between the polar groups and the metal halides resulting in the shift of the electrons in the double bond of the complexed monomers.



Direction of Shift of Electron Density

Arita et al³⁶) showed that the copolymerization of acrylonitrile with styrene was initiated by the addition of $ZnCl_2$ to give rise to a copolymer with alternating tendency. They concluded that the complex formation with $ZnCl_2$ changed the values of Q and e of acrylonitrile. Therefore the alternating tendency may be due to the large difference of Q and, especially, e values between the complexed acrylonitrile and styrene. Monomers such as allylic compounds, for example, allyl alcohol and allyl acetate, which are poorly responsive in free radically initiated copolymerization, are more readily copolymerized with methyl methacrylate or acrylonitrile in the presence of $ZnCl_2$ ³⁷). The increased reactivity of allylic monomers may be due to the decreased degradative chain transfer or the conversion of degradative to effective chain transfer³⁸.

The effect of metal compounds in Lewis acid copolymerization is shown in Table 9. The aluminium compounds containing both alkyl and halogen groups are very effective in producing 1 : 1 alternating copolymer. Metal halides such as $SnCl_4$ and $TiCl_4$, and organo metallic compounds such as diethyl zinc and triethyl boron are inactive as catalysts. These observations suggest that coexistence of organic group and halogen incorporated with aluminium is important.

TABLE 9
Effect of Lewis Acids on the Copolymerization of
Propylene and Acrylonitrile

Monomer Pr.	(g) AN	Metal compounds (m. mole)	Yield (g)	(n) (dl/g)	N%
100	2.00	$AlEt_3$	50	0	—
100	2.00	$AlEt_2Cl$	50	0.67	—
100	2.00	$AlEt_{1.5}Cl_{1.5}$	50	2.24	14.83
100	2.00	$AlMe_{1.5}Cl_{1.5}$	50	1.29	14.88
100	2.00	$AlMe_{1.5}Br_{1.5}$	50	0.51	8.68
100	2.00	$Al(i-Bu)Cl_2$	50	1.33	0.25
100	2.00	$AlCl_3$	50	—	0
100	2.00	$SnCl_4$	50	0	—
100	2.0g	$TiCl_4$	50	0	—
30	2.00	$ZnEt_2$	50	0	—
30	1.00	BEt_3	32	0	—

34. J. C. Arthur, Jr. and F. A. Blovin, *J. Appl. Polym. Sci.*, **8**, 2813 (1964).
35. M. Imoto, T. Ohtsu and M. Nakabayashi, *Makromol. Chem.*, **65**, 194 (1963).
36. K. Arita et al, paper presented at 16th Discussion Meeting on Macromolecules, *Soc. of Polym. Sci. of Japan*, Fukuoka, II, B, 04 (1969).
37. M. Imoto et al, *Makromol. Chem.*, **82**, 277 (1966).
38. V. P. Zubov and M. B. Lachnov, *J. Polym. Sci.*, C, **23**, 147 (1967).
39. N. G. Gaylord and A. Takahashi, *J. Polym. Sci.*, **B6**, 743 (1968).
40. T. Ikegami and H. Hirai, *J. Polymer Sci.*, A-1, **8**, 195 (1970).
41. H. Hirai and M. Komiyama, *ibid.*, *Polymer Chem. Ed.* **12**, 2701 (1974).