Studies on Charge-Transfer Complex and Polymerization. XX. Terpolymerizations with the Anethole–Maleic Anhydride Alternating Copolymerization System

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ABSTRACT: Terpolymerizations of an anethole (M_1) and maleic anhydride (M_2) monomer pair with β-chloroethyl methacrylate, methacrylonitrile, or acrylonitrile (M_3) were found to give a polymer in which the ratio of $m_1:m_2$ was always 1. These results suggest that M_1 and M_2 are entering the polymerization reaction as a charge-transfer complex. The reactivity of the charge-transfer complex between anethole and maleic anhydride was evaluated and is discussed in terms of monomer reactivity ratios, r_1(complex) and $r_2(M_3)$. The e value obtained for the complex suggests that it is attacked on the donor side by the propagating radical to yield a maleic anhydride radical.

Bartlett and Nozaki initially suggested the concept that a charge-transfer complex formed between a donor and an acceptor monomer played an important role in alternating radical copolymerization.[1] Later, several authors supported this proposal.[2] However, some points of controversy[3] remained until the participation of the charge-transfer complex in the cross-propagation steps of the alternating copolymerization was demonstrated by application of a terpolymerization technique. We determined that the Alfrey–Goldfinger equation was not applicable to these terpolymerizations.[4] Moreover, dilution effects explicable exclusively by the complex mechanism but not by a free-propagation mechanism[5] were observed. Additional support for the complex mechanism was obtained from studies of copolymerizations of butadiene with maleic anhydride or sulfur dioxide (SO_2). The microstructure of butadiene units in the resulting alternating copolymer was rich in *cis*-1,4 structure (for example, 73.7% in maleic anhydride at 60° and 45.2% in SO_2 at 0°) in contrast with the cases of homopolymerization and copolymerization with conventional vinyl monomers (20% *cis*-1,4). The butadiene monomer was therefore considered to be maintained in a largely cisoid form in the monomeric state by complexation with maleic anhydride or SO_2 and that these complexes polymerize to give alternating copolymers.[6] Recently, we discussed possible relationships between the equilibrium constants of the charge-transfer complex formation and their reactivities in radical polymerization in the case of vinyl ether (1,2-dimethoxyethylene, β-chloroethyl vinyl ether, and *p*-dioxene)–maleic anhydride alternating copolymerization systems.[7] It was found that the larger the equilibrium constant of the complex formation, the higher was the reactivity of the complexes.

In this report, we selected anethole as the donor monomer. As other vinyl ethers, anethole does not homopolymerize *via* a radical mechanism, but can copolymerize with many other vinyl monomers, especially with maleic anhydride, to give an alternating copolymer. Its charge-transfer interaction with maleic anhydride is evidenced by the formation of a characteristic yellow color upon mixing these components.

Reactivities of the anethole–maleic anhydride complex were evaluated from three terpolymerizations using acrylonitrile, methacrylonitrile, and β-chloroethyl methacrylate as third monomers. These reactivities are discussed in the framework of the charge-transfer complex mechanism.

Experimental Section

Preparation and Purification of Monomers. Commercial grade anethole (ANE) and maleic anhydride (MAnh) were carefully distilled under reduced pressure. Acrylonitrile (AN) and methacrylonitrile (MAN) were dried over calcium hydride and distilled just before use. β-Chloroethyl methacrylate (CEMA) was prepared by transesterification as follows.

In a 500 ml two-necked round-bottomed flask having a capillary ebullator tube in one neck and a simple distillation column in the other were placed 60 g of ethylene chlorohydrin (ECH), 150 g of methyl methacrylate (MMA), 5 g of hydroquinone, and 3 g of *p*-toluenesulfonic acid. The solution was heated to boiling in an oil bath. During the heating, methanol distilled at 64~74° as an azeotropic mixture with MMA. When the rate of production of methanol had become very slow (8 hr), excess MMA, unreacted ECH, and CEMA were distilled under reduced pressure in that order. The crude CEMA was redistilled one or more times to give about 20 g of pure CEMA (49.0° (4 mm)). *Anal.* Calcd for $C_6H_9O_2Cl$: Cl, 23.86. Found: Cl, 23.59.

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TABLE I
TERPOLYMERIZATION OF ANE–MAnh–CEMA AT 60° [a]

AMC, no.	Feed, mol % ANE	Feed, mol % MAnh	Feed, mol % CEMA	Polymrzn time, min	Yield, %	Cl, %	Polym composn [b] (CEMA mol %)
1	33.3	33.4	33.3	40	5.3	11.41	43.2
2	10.0	10.0	80.0	16	2.5	22.43	92.9
3	14.9	15.0	70.1	15	2.1	20.90	85.4
4	45.1	44.9	10.1	32	5.8	2.57	9.1
5	9.9	80.0	10.1	18	3.2	6.25	22.7
6	45.2	10.0	44.8	63	4.1	18.22	72.8
7	79.8	10.1	10.1	53	1.7	4.41	15.8
8	10.1	44.9	45.0	29	5.6	17.98	71.7
9	15.0	59.9	25.1	31	6.3	10.00	37.4
10	60.1	14.9	25.0	81	4.3	10.10	37.8

[a] 20 mmol of monomer, 10 mg of AIBN, and 1.3~2.8 ml of benzene; total volume is 4.00 ml. [b] Calculated from per cent chlorine on assumption of ANE/MAnh = 1.

TABLE II
TERPOLYMERIZATION OF ANE–MAnh–MAN AT 60° [a]

AMM no.	Feed, mol % ANE	Feed, mol % MAnh	Feed, mol % MAN	Polymzn time, min	Yield, %	N, %	Polym composn [b] (MAN mol %)
1	33.4	33.3	33.3	150	2.8	2.51	20.0
2	10.0	10.0	80.0	848	3.1	15.1	82.8
3	14.9	14.9	70.2	847	4.6	12.1	71.6
4	44.9	44.8	10.3	40	2.9	0.44	3.8
5	60.0	20.1	19.9	176	3.1	1.13	9.5
6	10.1	45.0	44.9	447	1.4	8.56	56.1
7	20.0	59.9	20.1	80	1.0	1.76	14.5
8	45.1	10.0	44.9	597	2.4	6.02	42.6
9	50.1	25.0	24.9	159	3.0	1.58	13.0
10	24.9	49.8	25.3	145	2.1	1.90	15.5

[a] 20 mmol of monomer, 10 mg of AIBN, and 1.5~2.3 ml of benzene; total volume is 4.00 ml. [b] Calculated from per cent nitrogen on assumption of ANE/MAnh = 1.

Benzene for use as a polymerization solvent was purified by washing with concentrated sulfuric acid, refluxing over sodium metal, and distilling.

Polymerization Procedure. Given amounts of azobisisobutyronitrile initiator, monomers (MAnh, ANE, and M_3), and benzene were weighed into ampoules in that order. The ampoules were flushed with nitrogen and sealed. Polymerization was accomplished by heating without stirring in an oil bath at 60 ± 0.2°. After a given time of polymerization, the ampoules were opened, a small amount of hydroquinone–benzene solution was added to the reaction mixture, and it was poured into excess ethyl ether (dried over sodium metal). The white, powdery polymers were obtained by drying *in vacuo* after repeated washings with anhydrous ethyl ether.

Calculation of Feed and Polymer Composition. Feed concentrations of monomers were calculated from the weights of components and their specific gravities (ANE 0.985, MAnh 1.40, CEMA 1.113, MAN 0.800, AN 0.806, benzene 0.876). In the determination of polymer compositions, the amount of AN or MAN units present was calculated by nitrogen analysis, and CEMA unit content by chlorine analysis. This procedure assumes that ANE and MAnh would be incorporated equally into the terpolymer *via* the complex mechanism. This assumption was confirmed by carbon and hydrogen analyses.

Spectrophotometric Measurements. Determination of the equilibrium constant for complex formation between ANE and MAnh was performed with a Hitachi Perkin-Elmer 139 uv-visible spectrophotometer using 0.5-cm Pyrex cells and a thermostated cell holder by the previously described procedure.[7]

Results and Discussion

Polymerization Behavior. In Tables I, II, and III are shown the results of three terpolymerizations of ANE–MAnh–M_3, where M_3 is CEMA, MAN, or AN, respectively. Table IV shows the alternating tendency of the ANE and MAnh fraction in the terpolymers obtained. In the last two columns are shown carbon and hydrogen percentages of the ANE–MAnh parts, calculated by deducing the amounts of M_3 fractions from the total terpolymer content and correcting the deviation due to absorbed water. Since carbon contents of ANE and MAnh are considerably different from each other (81.05 and 48.99 wt %, respectively), good agreement between the per cent carbon in the ANE–MAnh portion and the theoretical value of a 1:1 copolymer of ANE and MAnh (68.28 wt %) supports the perfectly alternating character between ANE and MAnh in the terpolymers.

Application of the Alfrey–Goldfinger Treatment of Terpolymerization. In a terpolymerization of three monomers M_1, M_2, and M_3, nine different elementary chain propagation steps, whose rate constants are denoted as k_{ij} ($i,j = 1 \sim 3$), must be considered. In the ANE–MAnh–M_3 systems, because ANE and MAnh

TABLE III
TERPOLYMERIZATION OF ANE–MAnh–AN AT 60°[a]

AMA no.	Feed, mol %: ANE	MAnh	AN	Polymrzn time, min	Yield, %	N, %	Polym composn[b] (AN mol %)
12	25.3	26.1	48.6	40	5.3	1.45	11.6
15	16.1	16.9	67.0	70	6.0	3.19	24.3
18	19.1	60.0	20.9	25	3.8	0.43	3.7
19	15.3	13.9	70.8	90	5.1	4.06	29.8
20	13.6	28.4	58.0	70	4.7	2.34	18.3
26	5.6	51.3	43.1	55	3.9	2.70	20.7
29	36.6	17.2	46.2	60	4.5	1.55	12.6
32	6.4	14.9	78.7	85	4.9	4.69	34.2
33	58.9	10.1	31.0	120	4.0	1.37	11.4
36	13.3	73.0	13.7	30	4.4	0.32	2.7

[a] Bulk polymerization; 0.1 mol % AIBN. [b] Calculated from per cent nitrogen on assumption of ANE/MAnh = 1.

TABLE IV
ALTERNATING CHARACTER OF ANE AND MAnh IN TERPOLYMERS

No.	Copolymer, %: Cl or N	C	H	ANE–MAnh part of copolymer,[a] %: C	H
AMC-3[b]	20.90	49.00	6.28	64.75	9.26
5	6.25	61.36	6.01	67.86	6.15
8	17.98	52.96	6.24	67.29	6.72
10	10.10	58.94	6.26	67.55	6.46
AMM- 5	1.13	68.08	6.46	67.89	6.40
6	8.56	68.40	6.96	67.31	6.51
8	6.02	70.07	6.97	69.45	6.74
10	1.90	67.47	6.38	67.68	6.23
AMA-15	3.19	68.64	6.05	68.74	6.10
19	4.06	68.57	6.22	68.70	6.31
29	1.55	68.24	5.69	68.26	5.69
36	0.32	67.15	5.75	68.17	5.67

[a] The values are corrected for deviations arising from absorbed water. Theoretical values for a 1:1 copolymer of ANE and MAnh are: C, 68.28, H, 5.73, and O, 25.99 (*cf.* ANE: C, 81.05; MAnh: C, 48.99). [b] The analytical error is relatively large, because the number of ANE–MAnh groups in the terpolymer is small.

TABLE V
MONOMER REACTIVITY RATIO IN BINARY COPOLYMERIZATIONS[a]

System: M_1	M_2	Monomer reactivity ratio: r_1	r_2
ANE	CEMA	0.0258 ± 0.0069	23.3 ± 1.7
	MAN	0.17 ± 0.18	4.6 ± 1.1
	AN	0.00570 ± 0.00046	0.306 ± 0.011
MAnh	CEMA	0.00386 ± 0.0026	5.32 ± 0.38
	MAN	−0.0017 ± 0.0024	18.1 ± 1.4
	AN	0[b]	6[b]

[a] 0.02 mol of monomer, 10 mg of AIBN, and about 2 ml of benzene; total volume is 4.00 ml. [b] F. R. Mayo, F. M. Lewis, and C. Walling, *J. Amer. Chem. Soc.*, **70**, 1529 (1948).

have a vanishingly small rate of self propagation ($k_{11} = k_{22} = 0$), Alfrey–Goldfinger equations for these terpolymerizations take the following form[8]

$$\frac{m_1}{m_2} = \frac{M_1\left[\frac{R_2M_3}{r_{31}} + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}}\right][R_1M_3 + M_2]}{M_2\left[\frac{R_1M_3}{r_{31}} + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}}\right][R_2M_3 + M_1]}$$

$$\frac{m_1}{m_3} = \frac{M_1\left[\frac{R_2M_3}{r_{31}} + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}}\right][R_1M_3 + M_2]}{M_3[R_1M_1 + R_1R_2M_3 + R_2M_2]\left[M_3 + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}}\right]} \quad (1)$$

$$\frac{m_2}{m_3} = \frac{M_2\left[\frac{R_1M_3}{r_{32}} + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}}\right][R_2M_3 + M_1]}{M_3[R_1M_1 + R_1R_2M_3 + R_2M_2]\left[M_3 + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}}\right]}$$

where r_{32}, r_{31}, R_1, and R_2 are equal to k_{33}/k_{32}, k_{33}/k_{31}, k_{13}/k_{12}, and k_{23}/k_{21}, respectively.

While r_{32} and r_{31} can be obtained from binary copolymerizations of M_3 with M_2 and M_1 (Table V), R_1 and R_2 can only be obtained by application of eq 1 to terpolymerization results. In Table VI are shown the calculated values of R_1 and R_1. Increasing the feed concentration of M_3 is found to decrease the R_1 value, over a wide range. R_1 and R_2, as calculated, are not unique values, but are scattered, in contradistinction to their theoretical constancy. These results suggest that the Alfrey–Goldfinger equation, based on a free propagation mechanism, is not applicable to a terpoly-

TABLE VI
APPLICATION OF THE ALFREY–GOLDFINGER EQUATION TO THE ANE–MANH–M_3 SYSTEM

No.	Feed, mol %: ANE	MAnh	M_3	R_1[a]	R_2[a]
AMC-3	14.9	15.0	70.1	−0.26	−1.17
7	79.8	10.1	10.1	0.048	0.72
10	60.1	14.9	25.0	0.002	0.05
AMM-2	10.0	10.0	80.0	−0.02	0.08
6	10.1	45.0	44.9	0.16	0.11
8	45.1	10.0	44.9	0.003	0.36
AMA-18	19.1	60.0	20.9	0.53	−0.10
29	36.6	17.2	46.2	0.002	0.22
32	6.4	14.9	78.7	0.005	0.022

[a] $R_1 = k_{13}/k_{12}$ and $R_2 = k_{23}/k_{21}$, where M_1 and M_2 are ANE and MAnh, respectively.

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TABLE VII
MONOMER REACTIVITY RATIO OF THE ANE–MAnh–M_3 SYSTEM AS A COPOLYMERIZATION OF THE ANE–MAnh COMPLEX WITH M_3[a]

System	Modified monomer reactivity ratios[b] r_1K and (r_2/K)	r_1(complex) and $(r_2(M_3))$	r_1r_2
ANE–MAnh–CEMA	0.495 ± 0.028	11.5 ± 1.2	~1
	(2.21 ± 0.22)	(0.095 ± 0.014)	
ANE–MAnh–MAN[c]	1.280 ± 0.048	29.8 ± 2.6	0.82
	(0.64 ± 0.15)	(0.028 ± 0.008)	
ANE–MAnh–AN	1.937 ± 0.027	45.0 ± 2.9	0.31
	(0.162 ± 0.047)	(0.0070 ± 0.0024)	
ANE–MAnh–VDC	2.30 ± 0.15	53.5 ± 6.1	0.32
	(0.14 ± 0.12)	(0.0060 ± 0.0055)	

[a] Polymerization temperature, 60°. [b] K = 0.0430 ± 0.0021 l./mol at 60° (Table VIII). [c] Calculated from the data corresponding to monomer feeds of [ANE] ≥ [MAnh].

TABLE VIII
EQUILIBRIUM CONSTANT OF CHARGE-TRANSFER COMPLEX FORMATION BETWEEN ANE AND MAnh[a]

Temp, °C[b]	$1/K\epsilon$, mol² cm/l.²	$1/\epsilon$, mol cm/l.	K,[d] l./mol
8.5	0.008394 ± 0.000079	0.000578 ± 0.000203	0.0665 ± 0.0038
21.9	0.009452 ± 0.000066	0.000570 ± 0.000169	0.0589 ± 0.0033
50.8	0.01208 ± 0.000079	0.000527 ± 0.000141	0.0462 ● 0.0025
		Mean 0.000558 ± 0.000027[e]	
60.0			0.0430 ± 0.0021[e]

[a] Determined by the Benesi–Hildebrand relation $[MAnh]\cdot l/d = (1/K\epsilon)1/[ANE] + 1/\epsilon$ using the absorption at 380 mμ at a concentration of [MAnh] = 0.025 and [ANE] = 0.20~1.80 mol/l. (l, path length; d, absorbance due to complex. $[MAnh]\cdot l/d$ *vs.* 1/[ANE] was plotted to give slope, $1/K\epsilon$, and intercept, $1/\epsilon$). [b] ±0.5. [c] Used in order to calculate K in combination with $1/K\epsilon$. [d] Thermodynamic constants of complex formation were determined as follows: $-\Delta H$ = 1.59 kcal/mol, ΔG = 1.66 kcal/mol, $-\Delta S$ = 11.0 eu at 21.9°. [e] Determined by plotting log K *vs.* $1/T$.

merization including two monomers (M_1 and M_2) which have a strong interaction tendency, such as charge-transfer complexation. Similar ineffectiveness of the Alfrey–Goldfinger equation has been observed in the dodecyl vinyl ether–fumaronitrile–β-chloroethyl acrylate system.[4]

Complex Mechanism Treatment of Terpolymerizations. A terpolymerization, in which a donor and an acceptor monomer are alternatingly incorporated into polymer chains, can be regarded as a binary copolymerization of a molecular complex between a donor and an acceptor monomer with a molecule of a third monomer. Evaluation of the polymerization behavior of the molecular complex is performed by determining an equilibrium constant, K, for complex formation and using this value to estimate [C]([C] ≒ K[D][A]) in the Mayo–Lewis equation (eq 2).

$$-\frac{d[C]}{d[M_3]} = -\frac{d[D] \text{ or } d[A]}{d[M_3]} = \frac{[D][A]}{[M_3]} \times \left\{\frac{r_1K[D][A] + [M_3]}{[D][A] + (r_2/K)[M_3]}\right\} \quad (2)$$

From eq 2, modified monomer reactivity ratios, r_1K and r_2/K, can be calculated. In Table VII these values for three terpolymerization systems and the ANE–MAnh–vinylidene chloride (VDC) system are shown. The corresponding copolymerization curves are illustrated as in Figure 1. To determine the monomer reactivity ratios r_1(complex) and $r_2(M_3)$, the equilibrium constant, K, of the complex formation between ANE and MAnh is necessary and was evaluated according to Benesi–Hildebrand method (see footnote *a* of Table VIII). The K value at 60° (polymerization temperature) has been estimated to be 0.0430 ± 0.0021 l./mol by plotting log K *vs.* $1/T$. Products of the monomer reactivity ratios, r_1(complex)·$r_2(M_3)$, are not more than unity and thus are not inconsistent with a normal free-radical copolymerization.

Reactivity of the Charge-Transfer Complex. According to the complex mechanism, the complex must have a very high reactivity for polymer radicals in the case of the ANE–MAnh–M_3 systems, because ANE and MAnh are always incorporated equally into polymer chains and consumed at higher rates than M_3. The reactivity ratios r_1 and r_2, obtained by the above method, are summarized in Table VII. The reactivity of M_3 toward the complex radical ($k_{\text{complex}\cdot M_3}$) was found to decrease in the order CEMA > MAN > AN > VDC. Since the polymer radical of the terminal complex unit has an electron-accepting character (see below), this order, with the exception of VDC, was expected from e and e' values of M_3 (Table IX). The

TABLE IX
Q, e VALUES OF M_3 AND MAnh[a]

Monomer	Q	e	Q'	e'
CEMA[b]	0.69	0.62	3.47	1.42
MAN	1.12	0.81	3.33	1.74
AN	0.60	1.20	2.70	1.91
VDC	0.22	0.36	0.48	1.09
MAnh	0.23	2.25		

[a] Q', e' correspond to case II in Table XII. [b] Calculated from the copolymerization with styrene (M_2): r_1 = 0.288 ± 0.010, r_2 = 0.462 ± 0.033.

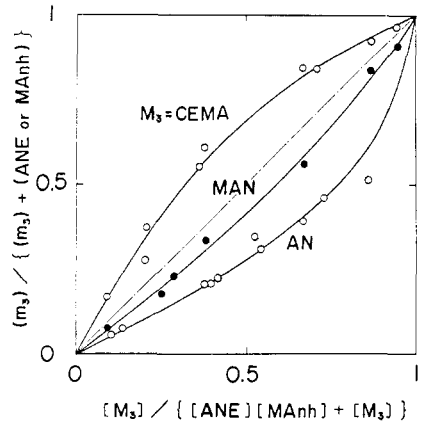

Figure 1. Copolymer composition diagram of ANE–MAnh–M_3 systems as binary copolymerizations between ANE–MAnh complex and M_3.

smaller reactivity of VDC with respect to the other monomers is considered to be the result of its Q and Q' value. In Table X, the reactivities of the complexes calculated from Table VII and V are shown in ratios of $k_{A\cdot complex}/k_{A\cdot B}$ (B denotes ANE and MAnh monomer), indicating, for instance, that the reactivity of the complex toward the polymer radical having a terminal unit of CEMA (A) is about 250 times as large as that of free ANE monomer. The variation of the ratios $k_{A\cdot complex}/k_{A\cdot B}$ on radical species A is thought to be mainly due to the variation in $k_{A\cdot B}$. It is possible that the variation of $k_{A\cdot B}$ on the three radicals is considered to have different directions in respective cases of monomer species B since ANE and MAnh are a donor and an acceptor monomer, respectively, while the variation of $k_{A\cdot complex}$ on radical species A should be in a given direction regardless of monomer species B.

Now, we must consider the possibility of a choice of direction of opening the complex for attack by a polymer radical

$$R\cdot + \text{complex} \longrightarrow R\text{-(ANE)-(MAnh)}\cdot$$
$$R\cdot + \text{complex} \longrightarrow R\text{-(MAnh)-(ANE)}\cdot$$

Table XI, in which reactivity ratio $k_{A\cdot A}/k_{A\cdot B}$ of the ten kinds of polymer radicals toward three monomers (MMA, MAN, and AN) are summarized, shows that the polymer radical produced from the ANE–MAnh complex has an electron-accepting property, since its order of reactivity toward the three monomers is similar to polymer radicals produced from vinyl monomers having positive e values. Therefore, this suggests that, when the complex has been attacked by a polymer radical, a polymer radical with a terminal MAnh unit is obtained rather than that of ANE. The same proposal has been made in a case of the vinyl ether–MAnh system.[7,9]

Q and e Values of the Charge-Transfer Complex. In Table XII are shown Q and e values of the ANE–MAnh complex considered as a single monomer in three ways of treatment and in Table IX are shown those of M_3 and MAnh. Case I and II correspond to treatments based on e values of styrene of −0.8 and 0,[10] respectively. In addition, case III arises from the assumption that the complex may have a dual character, that is, when the complex may be attacked on the side of ANE by a polymer radical to rearrange ultimately to a polymer radical with a terminal MAnh unit, the electronic character in a monomeric state is considered to be ANE–monomerlike and that in a terminal radical state is MAnh–radicallike. Therefore, the e value of MAnh (2.25) could be adopted for the polymer radical of a terminal complex unit, and Q_1 and e_1 values of the

TABLE X
REACTIVITY OF THE ANE–MAnh COMPLEX TOWARD RADICALS ($k_{A\cdot complex}/k_{A\cdot B}$) CALCULATED FROM BINARY- AND TERNARY-COPOLYMERIZATION DATA (TABLE V, VII)

Radical, A	Monomer, B: ANE	Monomer, B: MAnh
CEMA	250 ± 60	56 ± 13
MAN	160 ± 90	650 ± 260
AN	43 ± 20	857

TABLE XI
RELATIVE REACTIVITY ($k_{A\cdot A}/k_{A\cdot B}$) OF POLYMER RADICALS FOR THREE MONOMERS SUCH AS MMA (OR CEMA), MAN, AND AN[a]

Polymer radical,[b] A (e value)	Monomer, B: MMA	MAN	AN
ANE–MAnh complex	11.5[c]	29.8	45.0
MMA (0.40)	1	0.67	1.35
MAN (0.81)	0.65	1	2.68
AN (1.20)	0.13	0.32	1
NVPF (2.12)	0.008	0.062[d]	0.20
2-VP (−0.50)	0.77	0.60[d]	0.47
4-VP (−0.20)	0.79	0.60[d]	0.41
NVCZ (−1.03)	0.20	0.058[d]	0.072[d]
St (−0.8)	0.54	0.30	0.40
α-MeSt (−1.27)	0.14	0.12	0.1

[a] The data not related to the complex were cited from "Copolymerization," G. E. Ham, Ed., Interscience Publishers, New York, N. Y., 1964. [b] NVPF, N-vinylpyridinium fluoroborate; VP, vinylpyridine; NVCZ, N-vinylcarbazole; St, styrene. [c] Value for CEMA monomer. [d] Calculated from the Q, e values of two monomers.

TABLE XII
Q, e VALUES OF THE ANE–MAnh COMPLEX CALCULATED FROM THREE TERPOLYMERIZATION SYSTEMS BY THREE METHODS

System		Case I[a]	Case II[b]	Case III[c]
ANE–MAnh–CEMA	Q	7.9	40	7.3
	e	0.62	1.42	0.62
ANE–MAnh–MAN	Q	28, 57	56	45
	e	0.35, 1.3	1.30	0.95
ANE–MAnh–AN	Q	24	50	320
	e	0.12	0.83	2.3

[a] Based on $Q = 1$, $e = -0.8$ of styrene. [b] Based on $Q = 1$, $e = 0$ of styrene. [c] Based on the assumption that the ANE–MAnh complex will ultimately rearrange to a MAnh radical by attack of polymer radicals.

(9) S. Iwatsuki, K. Nishio, and Y. Yamashita, *Kogyo Kagaku Zasshi*, **70**, 384 (1967).

(10) N. Kawabata, T. Tsuruta, and J. Furukawa, *Makromol. Chem.*, **51**, 70, 80 (1962).

complex in a monomeric state are calculated by the equations

$$r_1 = (Q_1/Q_2)\exp\{-e_1^*(e_1 - e_2)\}$$

$$r_2 = (Q_2/Q_1)\exp\{-e_2(e_2 - e_1)\}$$

where r_1 and r_2 are obtained experimentally by the copolymerization of the complex and M_3, e_1^* is the e value of the polymer radical of a terminal complex unit and equal to the e value of MAnh, and e_2 and Q_2 are those of M_3.

Q_1 and e_1 values of the ANE–MAnh complex vary largely with the nature of M_3 in case I and III, but they cluster at characteristic values and become independent of M_3 in case II (Table XII). However, this treatment in case III, considering a dual character of the complex, is considered to become more suitable when we could choose more proper Q and e values of M_3 and of MAnh.

The Q value of the complex is very large in comparison with those of conventional vinyl monomers, and similar results have been obtained in the case of Lewis acid complexes of polar vinyl monomers such as MMA, AN, etc.[11] Since the Q values are generally envisioned as a gain in resonance energy on going from a monomeric state to a radical state, the very large Q value of the complex corresponds to its pronounced reactivity.

Anomaly in the Terpolymerization System Including MAN. It can be pointed out in Table II and more clearly in Figure 2 that two kinds of monomer feeds, one of which is [ANE] = a, [MAnh] = b, and [MAN] = c (moles/liter) and the other is [ANE] = b, [MAnh] = a, and [MAN] = c, do not lead to the same composition of the terpolymers, even though alternating tendency of ANE and MAnh is continued. Moreover, when $a > b$, the former feed gives a terpolymer containing more complex units than the latter one. Since the relation [C] $\doteqdot$ K[D][A] may generally exist for a moderately small equilibrium constant, K, of complex formation between a donor, D, and an acceptor, A, and, also, simple exchange of monomer concentrations [D] for [A], does not lead to variation of [C], those two kinds of monomer feeds should give the same polymer composition. This anomaly from the theoretical consideration in the composition relationship between feeds and polymers could be explained in the following three ways. First a dependence

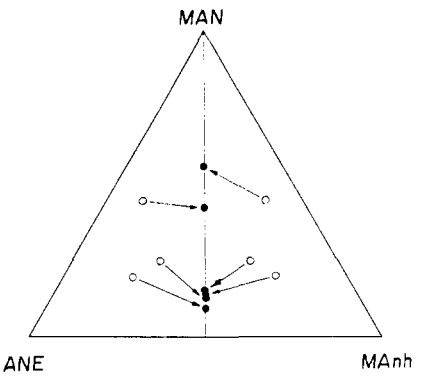

Figure 2. Trigonal composion diagram of ANE–MAnh–MAN system: ○, feed composition; ●, polymer composition.

of some property, such as polarity of the system, on feed composition could lead to a variation of reactivities of polymer radicals toward complex or M_3 as a result of differential solvation. The second is that the kinds of radicals produced from a complex may vary with feed composition, *e.g.*, a MAnh radical is probably obtained in the presence of excess MAnh rather than when an excess ANE is available. The third is that the K value may not always be constant in the whole range of feed composition. Ross and Labes[12] observed the dependence of K on the feed composition and rationalized this behavior by invoking formation of termolecular species such as AD_2 or A_2D. In addition, Foster, *et al.*,[13] observed that the K value varied with the wavelength used for measurement when [D] $\gg$ [A] rather than when [D] $\approx$ [A]. This anomaly was considered to arise from formation of termolecular species. Figure 2 shows that a MAN monomer unit is incorporated more readily into polymer chains when [ANE] < [MAnh] in monomer feed rather than when [ANE] > [MAnh]. As MAN has electron-accepting character, MAN is expected to be incorpoated into the copolymer chains with ease when [ANE] > [MAnh] rather than when [ANE] < [MAnh] *via* a free propagation mechanism. Therefore, this fact is hardly elucidated *via* the free propagation mechanism.

An entirely similar result has been observed in the isobutyl vinyl ether–MAnh–AN system and will be reported elsewhere.

(11) M. Imoto, T. Otsu, and Y. Harada, *Makromol. Chem.*, **65**, 180 (1963); M. Imoto, T. Otsu, and M. Nakabayashi, *ibid.*, **65**, 194 (1963), S. Yabumoto, K. Ishii, and K. Arita, *J. Polym. Sci., Part A-1*, **7**, 1577 (1969).

(12) S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, **79**, 76 (1957).

(13) R. Foster and I. Horman, *J. Chem. Soc. B*, 171 (1966); G. D. Johnson and R. E. Bowen, *J. Amer. Chem. Soc.*, **87**, 1655 (1965).