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Alternating Copolymerization of β-Cyanoacrolein with α-Methylstyrene

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Alternating copolymer was obtained in the system of β-cyanoacrolein (CAL) and α-methylstyrene (α-MeSt). In the presence of air copolymerization proceeds even without any radical initiator at room temperature. In the radical initiated copolymerization of α-MeSt (M_1) and CAL (M_2), the values of monomer reactivity ratios $r_1=0.033$ and $r_2=0$ were obtained. Neither the rate of copolymerization nor viscosity number of the copolymer formed were influenced by the presence of air in the reaction system. The result of copolymerization in the ternary system involving methyl acrylate (MA) could not be entirely explained by the copolymerization equation given by Alfrey and Goldfinger for the three component system. It was found that the composition of the copolymer formed changed with the solvent dilution. Formation of 1 : 1 molecular complex between the monomers was evidenced by the application of the continuous variation method to α-MeSt-CAL system. It was concluded that the molecular complex due to some donor-acceptor type interaction between CAL and α-MeSt plays an important role in the copolymerization.

In the radical copolymerization of β-cyanoacrolein (CAL) with styrene (St), the monomer reactivity ratios were determined and the result was discussed with consideration of penultimate effect.[1] The radical copolymerization of CAL with acrylonitrile was also investigated, compared with that in CAL-St system.[2] It was reported that CAL induced the polymerization of *N*-vinylcarbazole (VCZ) which was cationic polymerization induced by the donor-acceptor type interaction between CAL and VCZ.[3]

The present study is concerned with the alternating copolymerization of CAL with α-methylstyrene (α-MeSt).

1) H. Sumitomo and K. Azuma, *J. Polym. Sci. B*, **4**, 883 (1966).

2) I. Takemura and H. Sumitomo, This Bulletin, **42**, 634 (1969).

3) H. Sumitomo and I. Takemura, *ibid.*, **42**, 631 (1969).

Experimental

Materials. CAL was synthesized from β-cyanopropionaldehyde.[1] α-MeSt was washed successively with 5% aqueous solution of sodium thiosulfate, water, an aqueous solution of sodium hydroxide and water, and dried on anhydrous sodium sulfate. Methyl acrylate (MA) was purified by distillation. Benzoylperoxide (Bz_2O_2) was purified by reprecipitation in chloroform (solvent) methanol - (precipitant) system. Dioxane was distilled after refluxing with sodium. Tetrahydrofuran (THF) was also purified in the same way. Benzene was purified in the usual way.

Copolymerization. Copolymerization of CAL with α-MeSt was carried out in dioxane in an evacuated sealed tube at 80°C using Bz_2O_2 as an initiator. Copolymerization in the systems of CAL-MA, α-MeSt-MA and CAL-α-MeSt-MA were also conducted by the same method. The resulting copolymer was precipitated into a large excess of methanol. The copolymer thus isolated was purified by the precipitation from the system of tetrahydrofuran (solvent) - methanol (precipitant).

Table 1. α-MeSt - CAL copolymerization. Effects of solvent, radical initiator and air

Expt. No.	Monomer			Wt. ratio of dioxane monomer	Bz_2O_2 mol% to monomer	Atmosphere[a]	Temp. °C	Time hr	Convn. %	η_{sp}/c[b]	Mole fraction of α-MeSt in copolymer
	α-MeSt g	CAL g	Mole fraction of α-MeSt								
52	3.54	—	—	—	—	A	80	5	0	—	—
53	3.54	—	—	—	—	V	80	5	0	—	—
54	3.54	—	—	—	0.5	A	80	5	0	—	—
55	3.54	—	—	—	0.5	V	80	5	0	—	—
56	3.54	—	—	—	—	A	21—22	8	0	—	—
57	3.54	—	—	—	—	V	21—22	8	0	—	—
29	2.36	1.62	0.5	—	—	A	80	5	3.8	0.18	0.512
30	2.36	1.62	0.5	—	—	V	80	7	4.2	0.18	0.539
42	2.36	1.62	0.5	2	—	A	80	5	1.2	—	0.538
43	2.36	1.62	0.5	2	—	V	80	9	1.6	—	0.532
44	2.36	1.62	0.5	2	0.5	A	80	3	11.6	0.08	0.512
45	2.36	1.62	0.5	2	0.5	V	80	3	11.6	0.08[c]	0.508
58	2.36	1.62	0.5	—	—	A	21—22	8	0.3	—	—
59	2.36	1.62	0.5	—	—	V	21—22	8	0.2	—	—

a) A, air; V, vacuum.
b) THF, c=0.2 g/100 ml, 25°C.
c) M_n(VPO)=2380.

Determination of Polymer Composition. The compositions of the copolymers obtained in the systems of CAL - α-MeSt and CAL-MA were determined from nitrogen analysis by the Kjeldahl method. Those for α-MeSt - MA and α-MeSt - CAL - MA systems were determined by elemental analysis.

Measurement of Solution Viscosity. Viscosity number, η_{sp}/c, of a copolymer was measured at the concentration of 0.2g/100 m*l* in THF at 25°C with use of an Ostwald viscometer.

Nuclear Magnetic Resonance Spectrum. Nuclear magnetic resonance (NMR) spectrum was measured in carbon tetrachloride and carbon tetrachloride-methylene chloride mixture at 60°C with a Japan Electron Optics JNM-4H-100 spectrometer.

Continuous Variation Method. Continuous variation method applied to α-MeSt - CAL system was carried out in benzene using a quartz cell with a path length of 1 mm.

Results and Discussion

The results of the preliminary experiment of the copolymerization of CAL with α-MeSt are summarized in Table 1.

Although no homopolymerization of both CAL and α-MeSt takes place under the present conditions, copolymerization between them proceeds at room temperature in the presence of air even without any initiator.

The results of infrared analysis and the contents of α-MeSt in the products suggest the formation of 1 : 1 alternating copolymer of CAL with α-MeSt. The rate of copolymerization and the viscosity number of copolymer obtained are independent of the presence of air in the reaction system. This is curious from the view point of conventional free radical polymerization. In Figs. 1 and 2 are shown the results of copolymerization carried out in dioxane with benzoyl peroxide (Bz_2O_2) as an initiator at 80°C, with varying composition of

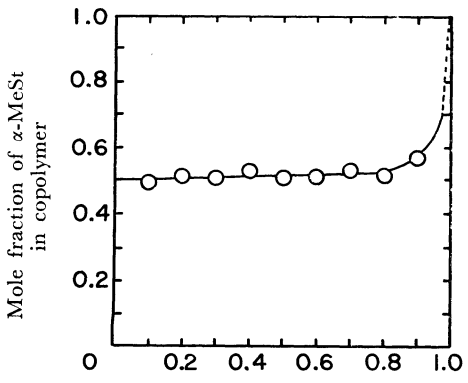

Fig. 1. Composition of copolymer as a function of monomer composition in α-MeSt (M_1) - CAL (M_2) system.
Solv., dioxane; initiator, Bz_2O_2; at 80°C.
○, Experimental value; —, Calculated from $r_1=0.033$ and $r_2=0$.

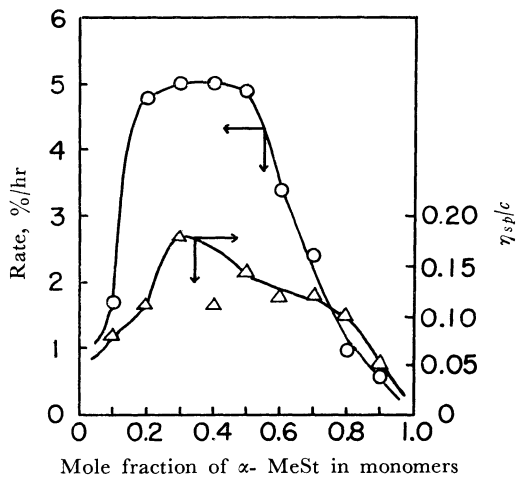

Fig. 2. Influence of monomer composition on the rate of copolymerization and on η_{sp}/c of copolymer in α-MeSt-CAL system.

monomer feed in the system of α-MeSt (M_1) and CAL (M_2).

As shown in Fig. 1, α-MeSt contents of the copolymer are 50 mol% within experimental error throughout the range of the monomer composition. There is a remarkable agreement between the experimental values and the curve calculated from the values of monomer reactivity ratios, $r_1=0.033$ and $r_2=0$. r_1 has a very small value and $r_2=0$, and the product r_1r_2 is nearly equal to zero. This means that both monomers have a very large alternating tendency.

The fact that the viscosity number of the copolymer has a maximum at the mole fraction of α-MeSt of about 0.40 indicates that there may be some interaction between CAL and α-MeSt as shown in Fig. 2. Q and e values obtained for the monomers are given in Table 2.

TABLE 2. Q-e VALUES

Monomer	Q	e
α-MeSt[a)]	0.98	−1.27
CAL[b)]	0.53	2.07

a) Ref. 4.
b) Obtained from copolymerization in CAL-St and CAL-AN systems.

Both monomers have large e values of the opposite sign. Thus some donor-acceptor type interaction is expected to take place between the monomers. In Table 3 is given the comparison of the monomer reactivity ratios between the observed values and those calculated from Q and e values.

Figure 3 shows the NMR spectra of poly α-MeSt (P α-MeSt) and the copolymer. In the spectrum

4) "Copolymerization," ed. by G. E. Ham, Interscience Publishers, New York (1964), p. 845.

Table 3. Parameters in α-MeSt (M_1) - CAL (M_2) system

	r_1	r_2	r_1r_2
Obsd	0.033	0	0
Calcd[a)]	0.026	0.0005	≅0

a) From Q-e value.

of P α-MeSt, the phenyl proton signal appears at the value 2.95—3.20, whereas the signal is seen as a singlet at 2.90 in the copolymer. The difference may be explained as follows. In P α-MeSt, the phenyl proton signal shifts to the higher field with splitting due to the shielding effect of the benzene ring in the sequence of α-MeSt unit. However, in the copolymer the shift is attributed to the alternation of CAL and α-MeSt units.

In the IR spectra of acrolein homopolymer and its copolymer with CAL, a weak C=O absorption band appears and there exist strong C–O–C absorption bands due to the substituted tetrahydropyrane ring formed between adjacent pendant aldehyde groups. On the other hand, the spectrum of the copolymer of CAL and α-MeSt indicates that aldehyde group remains free.[5)]

From these facts it seems that some interaction between CAL and α-MeSt plays an important role

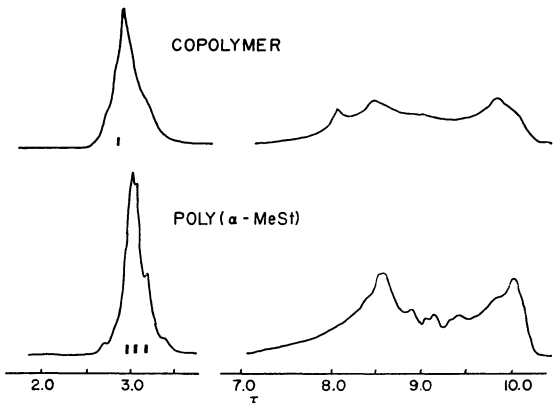

Fig. 3. NMR spectra of copolymer and poly-(α-methylstyrene).

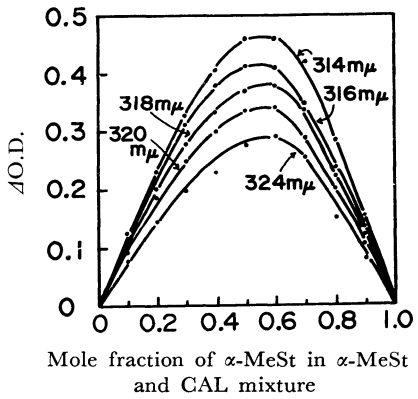

Fig. 4. Continuous variation method in α-MeSt and CAL system.
[CAL]=[α-MeSt]=0.5 mol/l; [CAL]+[α-MeSt] =0.5 mol/l; in benzene; path length, 0.1 cm.

Table 4. α-MeSt (M_1) - CAL(M_2) - MA (M_3) terpolymerization
Solv.: dioxane,[a)] Initiator: Bz_2O_2,[b)] Temp.: 80°C

Expt. No.	Monomer composition mole fraction			Time hr	Convn. %	Elemental analysis			Terpolymer composition mole fraction		
	α-MeSt	CAL	MA			C%	H%	N%	α-MeSt	CAL	MA
T-1	0.15	0.15	0.70	2	6.3	73.41	7.40	3.33	0.339	0.198	0.463
T-2	0.20	0.20	0.60	1	2.9	75.51	7.31	3.44	0.447	0.244	0.309
T-3	0.25	0.25	0.50	2	7.1	75.80	6.93	3.95	0.451	0.279	0.270
T-4	0.30	0.30	0.40	2	8.1	76.79	6.80	4.64	0.474	0.330	0.196
T-5	0.05	0.05	0.90	0.5	7.7	63.87	7.33	1.17	0.169	0.076	0.755
T-7	0.35	0.35	0.30	1	4.1	77.76	6.68	5.03	0.498	0.360	0.142
T-8	0.40	0.40	0.20	1	4.7	78.23	6.31	5.33	0.512	0.382	0.106
T-9	0.45	0.45	0.10	1	6.1	79.18	6.43	5.93	0.529	0.427	0.044
B-4	0.50	0.20	0.30	0.8	2.6	76.20	6.92	4.09	0.461	0.290	0.249
B-5	0.20	0.50	0.30	0.8	4.2	74.33	6.48	5.29	0.434	0.367	0.199
B-6	0.10	0.80	0.10	0.8	3.1	73.83	6.62	6.07	0.384	0.417	0.199
B-7	0.80	0.10	0.10	1.3	1.8	79.06	7.16	3.64	0.549	0.266	0.185
B-8	0.10	0.40	0.50	0.7	2.9	72.72	6.95	4.47	0.366	0.307	0.327
B-9	0.40	0.10	0.50	1	3.5	76.68	7.13	2.69	0.489	0.193	0.318
B-10	0.10	0.10	0.80	0.5	3.2	66.24	6.97	1.63	0.222	0.108	0.670

a) Dioxane/monomer = 2 (wt).
b) 0.5 mol%/Monomer.

5) Unpublished data.

in the alternating copolynerization in the system of CAL and α-MeSt. Although coloring was not observed when CAL was mixed with α-MeSt, an absorption maximum by the continuous variation method appeared at the molar ratio of CAL to α-MeSt of around one as shown in Fig. 4. This means that some molecular complex due to a donor-acceptor type interaction between CAL and α-MeSt was formed.

In Table 4 and Fig. 5 are summarized the results of terpolymerization including CAL, α-MeSt and methyl acrylate (MA).

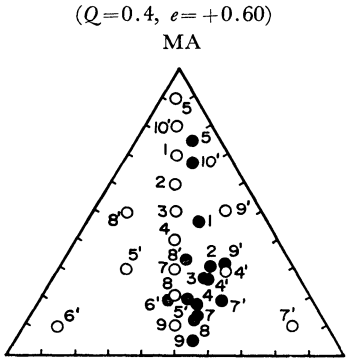

Fig. 5. Terpolymerization in α-MeSt - CAL - MA system.
Solv., dioxane; initiator, Bz_2O_2; at 80°C.
○, Composition in monomers;
●, Composition in terpolymer.

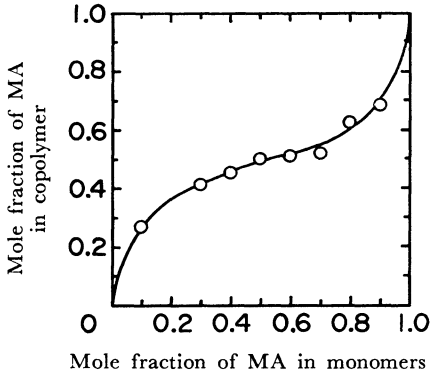

Fig. 6. Composition of copolymer as a function of monomer composition in MA (M_1)-α-MeSt (M_2) system.
Solv., dioxane; initiator, Bz_2O_2; at 80°C.
○, Experimental value; —, Calculated from $r_1=0.13$ and $r_2=0.21$

Deviation of the composition of terpolymer from the assumed copolymerization of 1:1 molecular complex of CAL and α-MeSt with MA, suggests that some interaction α-MeSt and MA may also take place other than that between α-

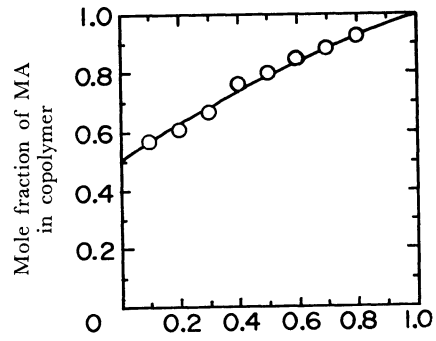

Fig. 7. Composition of copolymer as a function of monomer composition in MA (M_1)-CAL (M_2) system.
Solv., dioxane; intiator, Bz_2O_2; at 80°C.
○, Experimental value; —, Calculated from $r_1=2.73$ and $r_2=0$

MeSt and CAL. The following monomer reactivity ratios were determined in α-MeSt - MA and MA-CAL systems. The composition curve in these copolymerization systems are shown in Figs. 6 and 7.

MA (M_1) - α-MeSt (M_2), $r_1=0.13$ and $r_2=0.21$;
MA (M_1) - CAL (M_2), $r_1=2.73$ and $r_2=0$.

The Alfrey-Goldfinger's equation[6] was used for the anlaysis of the results in the ternary system. If k_{22} equals zero, since no homopolymerization of CAL occurs, the composition relationship in the ternary system is given as follows.

$$\frac{m_1}{m_2}=\frac{M_1}{M_2}\times\frac{(M_1+M_2/r_{12}+M_3/r_{13})(M_1/r_{31}+M_2/r_{32}+M_3/r_{31}R)}{(M_1+M_3/R)(M_1/r_{31}r_{12}+M_2/r_{32}r_{12}+M_3/r_{13}r_{32})}$$

$$\frac{m_1}{m_3}=\frac{M_1}{M_3}\times\frac{(M_1+M_2/r_{12}+M_3/r_{13})(M_1/r_{31}+M_2/r_{32}+M_3/r_{31}R)}{(M_1/r_{13}+M_2/r_{32}+M_3)(M_1/r_{13}+M_2/r_{12}R+M_3/r_{13}R)}$$

The value of R was determined from Q-e values, but not experimentally. Copolymerization parameters thus obtained are listed in Table 5.

Calculation of R using the results of terpolymerization and the binary copolymerization parameters gives $R\leqq 0$, except for B-6 and B-10. R calculated from the Q-e values is about 112 as shown in Table 5. If $R\cong 0$, it follows that $k_{21}\cong 0$ or $k_{21}\ll k_{23}$. Thus the relation $R=0$ should be discorded because it is inconsistent with the large alternating tendencies of CAL and α-MeSt, the reactivity of each monomer deduced from Q and e values and the existence of a donor-acceptor type interaction between CAL and α-MeSt. With respect to M_1 (mole fraction of

6) T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 332 (1944).

TABLE 5. COPOLYMERIZATION PARAMETERS IN α-MeSt (M_1) - CAL (M_2) - MA (M_3) SYSTEM

	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	$R=k_{21}/k_{23}$
Obsd	0.033	0	0.21	0.13	0	2.70	—
Calcd[a)]	0.026	0.0005	0.215	0.14	0.06	1.93	112

a) Calcd from the following Q-e values.
α-MeSt $Q=0.98$ $e=-1.28$
CAL $Q=0.53$ $e=2.07$
MA $Q=0.42$ $e=0.60$

α-MeSt in monomers) above 0.3, we have $R\cong 0$. If M_1 becomes smaller R tends to deviate gradually from zero. Deviation is very remarkable as to T-5 and B-8 where M_1 is very small. This shows that R changes with monomer composition. It is concluded that the equation proposed by Alfrey and Goldfinger can not be applied to the present ternary system.

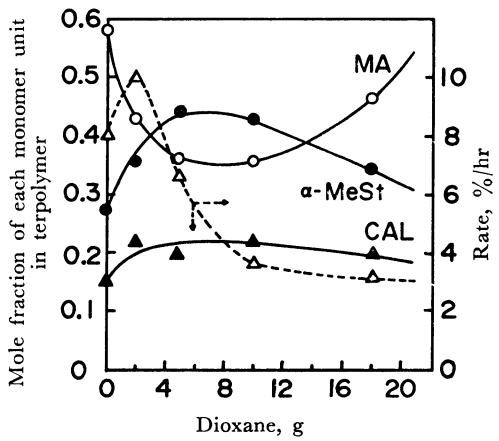

Fig. 8. Effect of solvent dilution on α-MeSt-CAL-MA terpolymerization.
Monomer composition, α-MeSt : CAL : MA = 1.5 : 1.5 : 7
Total amount of monomers, 8.02 g

The effect of solvent dilution on terpolymerization was investigated. The composition of the terpolymer varies with the amount of dioxane added as seen in Fig. 8. It should also be noted that a maximum of the rate appears with the addition of a small amount of the solvent.

This behavior is very different from that of general radical copolymerization, and can not be explained by the Alfrey-Goldfinger equation. Iwatsuki and Yamashita[7)] have discussed similar behaviors found in the systems of chloroethylvinylether-maleic anhydride-acrylonitrile and *p*-dioxene-maleic anhydride-acrylonitrile.

The change in the composition of terpolymer and the rate of copolymerisation seems to be much larger than the estimated values from the simple solvation effect of dioxane. Hence it appears that the interaction between each monomer would change with the addition of solvent and that species with different reactivities are formed in the system. The results show that the interaction between CAL and α- MeSt is very strong even in the terpolymerization. It is concluded that the complex formation between CAL and α-MeSt due to some donor-acceptor type interaction plays a very important role in the copolymerization system of CAL and α-MeSt.

7) S. Iwatsuki and Y. Yamashita, *J. Polym. Sci. A-1*, **5**, 1753 (1967).