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Copolymerization of β-Cyanoacrolein with Acrylonitrile

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Radical initiated copolymerization of β-cyanoacrolein (CAL, M_2) with acrylonitrile (M_1) in benzene at 60°C was investigated. The monomer reactivity ratios were determined to be $r_1=3.2$ and $r_2=0$. The copolymerization behavior is discussed in comparison with that in the system of styrene and CAL previously described. The Q and e values of CAL were also estimated to be 0.53 and 2.07, respectively, which were compared with those of other polar monomers.

In preceding papers,[1,2] the radical copolymerization of the new monomer, β-cyanoacrolein (CAL), with styrene (St) was investigated to give monomer reactivity ratios and to demonstrate the existence of a penultimate effect. It was also described that CAL induced the polymerization of *N*-vinylcarbazole even in air at room temperature and that there may be some donor-acceptor type interaction between *N*-vinylcarbazole and CAL in solution leading to initiate the cationic polymerization of *N*-vinylcarbazole.[2] The purpose of the present study is to determine the monomer reactivity ratios and Q-e values in the radical copolymerization of CAL with acrylonitrile (AN).

1) H. Sumitomo and K. Azuma, *J. Polymer Sci.*, **B4**, 883 (1966).
2) H. Sumitomo and I. Takemura, This Bulletin, **42**, 631 (1969).

Experimental

Materials. CAL was prepared according to the same method as that previously described.[1] Commercial AN was twice distilled in a stream of nitrogen after drying over potassium carbonate. Bp 77.0—77.3°C.

Table 1. $AN(M_1)$-$CAL(M_2)$ radical copolymerization[a)]

Expt. No.	Monomer AN(M_1) g	AN(M_1) mol	CAL(M_2) g	CAL(M_2) mol	Mol fraction of AN	Initiator[b)]	Time hr	Yield g	Conversion %	Copolymer composition[c)] mol fraction of AN
13	0.59	0.011	8.11	0.100	0.10	AIBN	18	0.12	1.40	0.608
36	1.06	0.020	6.48	0.080	0.20	Bz_2O_2	25	0.16	2.09	0.640
37	1.33	0.025	6.08	0.075	0.25	Bz_2O_2	20.5	0.19	2.55	0.673
38	1.59	0.030	5.67	0.070	0.30	Bz_2O_2	15	0.20	2.78	0.707
39	1.86	0.035	5.27	0.065	0.35	Bz_2O_2	12.5	0.26	3.61	0.757
33	2.12	0.040	4.86	0.060	0.40	Bz_2O_2	4.5	0.09	1.26	0.760
34	3.18	0.060	3.24	0.040	0.60	Bz_2O_2	1.5	0.11	1.70	0.860
35	4.24	0.080	1.62	0.020	0.80	Bz_2O_2	0.5	0.10	1.69	0.930
27	4.78	0.090	0.81	0.010	0.90	AIBN	0.25	0.16	2.93	0.971

a) In benzene at 60°C. The weight ratio of benzene to monomer, 2.
b) 0.5 mol% to monomer.
c) Determined by nitrogen contents by the Kjeldahl method.

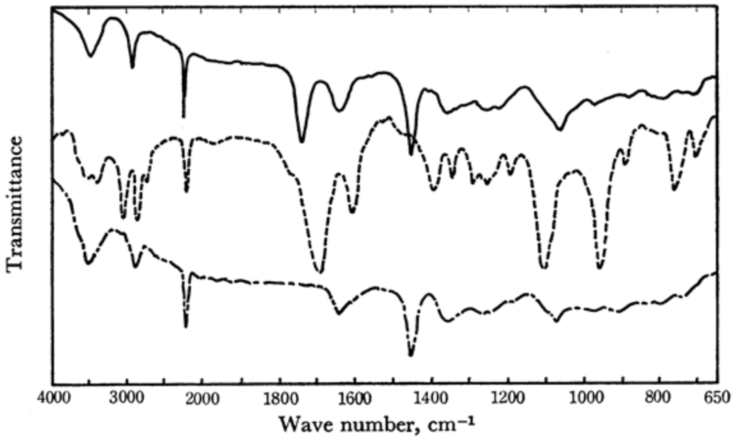


Fig. 1. Infrared absorption spectra of β-cyanoacrolein-acrylonitrile copolymer (solid curve), β-cyanoacrolein monomer (broken curve) and polyacrylonitrile (dot-dash-curve).

Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Benzoyl peroxide (Bz_2O_2) was purified by the reprecipitation from its chloroform solution into methanol. Benzene and dimethyl formamide (DMF) were purified in the usual way.

Polymerization. In a glass tube were placed initiator, CAL, AN and solvent in this order. The tube was sealed under vacuum after repeating freezing and thawing. Polymerization was conducted at 60±0.1°C. The resulting copolymer was precipitated in a larger amount of methanol and then purified by the reprecipitation in the system of DMF-methanol.

Copolymer Composition. The compositions of copolymers were determined from nitrogen contents by the Kjeldahl method.

Results and Discussion

The results of the copolymerization of AN (M_1) with CAL (M_2) are summarized in Table 1. Figure 1 shows the infrared absorption spectra of the copolymer, AN homopolymer and the CAL monomer.

In Fig. 2 are plotted the compositions of the initial copolymers against the initial monomer compositions. No homopolymerization of CAL was experimentally found to occur in the present condition. Hence the monomer reactivity ratio r_2 can be estimated at 0. The solid curve shown in Fig. 2 are drawn adopting values of $r_1=3.2$ and $r_2=0$ to the conventional Lewis-Mayo equation and it agrees very closely with the experimental data. Included in Fig. 2 for comparison is the data obtained in the previous St (M_1) - CAL (M_2) system.[1)]

There is a remarkable difference between the monomer reactivity ratios obtained in these copolymerization systems. The value of r_1 is larger than

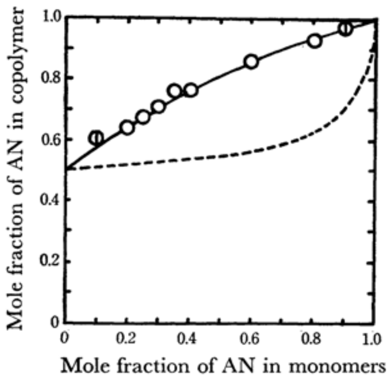
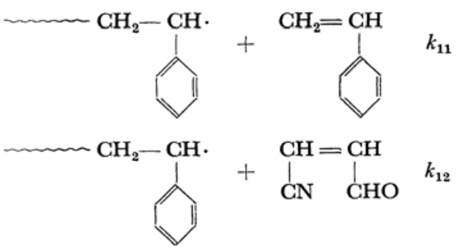


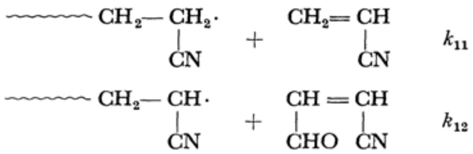
Fig. 2. Composition curve of St(M_1)-CAL(M_2) copolymerization ○, Bz_2O_2; ⦶, AIBN.
Solid curve, calculated by using $r_1=3.2$, $r_2=0$.
Broken curve shows St(M_1)-CAL(M_2) system ($r_1=0.09$; $r_1'=0.27$; $r_2=r_2'=0$).[1)]

unity in the AN (M_1) - CAL (M_2) system, whereas $r_1<1$ in the system of St (M_1) - CAL (M_2).

It has also been noticed in our experiments that, for example, the mixture of equal moles of St and CAL gives the copolymer at 5.7% conversion in 5.2 hr at 60°C, even in air without any other initiator. It is conceivable that there may be some donor-acceptor type interaction between St and CAL.



In the present copolymerization system, it may be suggested from the r_1 value that there exists stronger repulsion being attributed to the polar substituted groups between the growing AN radical and the coming CAL monomer rather than the AN monomer.



The values of Q and e for CAL calculated from the copolymerization data are shown in Table 2. Table 2 also includes the Q-e values for the related polar monomers.

TABLE 2. THE Q-e VALUES OF POLAR MONOMERS

Monomers		Q	e	Ref.
Maleic anhydride	HC = CH O=C–O–C=O	0.23	2.25	3)
CAL	NC–CH=CH–CHO	0.53	2.07	This paper
Fumaronitrile	NC–CH=CH–CN	0.80	1.96	3)
Acrylonitrile	CH_2=CH–CN	0.60	1.20	3)
Acrolein	CH_2=CH–CHO	0.85	0.73	3)

It can be seen from the e values in Table 2 that the polar effect of substituted groups in CAL is comparable with that in fumaronitrile, larger than that in AN and acrolein, and smaller than that in maleic anhydride.

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