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Kurzmitteilung

## Determination of $Q, e$ Parameters for Methyl $\alpha$ -Cyanoacrylate

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In the previous papers<sup>1-3</sup>, we have investigated the effects of alkyl groups in alkyl acrylates and methacrylates on their radical copolymerizations with styrene. On the other hand, the effects of  $\alpha$ -substituents in methyl acrylate were also reported by TSURUTA *et al.*<sup>4</sup> and CAMERON *et al.*<sup>5</sup>.

It is well known that methyl  $\alpha$ -cyanoacrylate is quite readily polymerized anionically by weak bases such as water. Owing to this reason, no detailed study on its radical polymerization and copolymerization has been appeared in the literature. Since some acidic materials such as acetic acid and sulfur dioxide have been used as inhibitors for methyl  $\alpha$ -cyanoacrylate, the presence of these materials in the polymerizing mixture would make it possible to analyze the radical polymerization of this monomer.

The present paper describes the accurate determination of  $Q, e$  parameters for methyl  $\alpha$ -cyanoacrylate from its radical copolymerization with methyl methacrylate in the presence of a small amount of acetic acid.

### Experimental

Methyl  $\alpha$ -cyanoacrylate (supplied by Taoka Dye Co.) was purified by fractional distillation under a reduced pressure in a stream of nitrogen containing sulfur dioxide as an inhibitor. In this case, the middle fraction was introduced into a known amount of acetic acid. Methyl methacrylate was used after purification by ordinary method and distillation before use.  $\alpha, \alpha'$ -Azobisisobutyronitrile (AIBN) as an initiator was recrystallized three times from ethyl alcohol.

Bulk copolymerizations of methyl  $\alpha$ -cyanoacrylate ( $M_1$ ) with methyl methacrylate ( $M_2$ ) were carried out in a sealed tube at 60°C in the presence of a small amount of acetic acid ( $[\text{AcOH}]/[M_1] = 6.1 \cdot 10^{-2}$  in molar ratio). After the copolymerization to *ca.* 5% conversion, the content of the tube was poured into a large amount of diethyl ether to isolate the copolymer. The resulting copolymer was then purified by reprecipitation from acetone-methanol or dimethylformamide-methanol system.

The composition of the copolymer was determined from its carbon content, from which the monomer reactivity ratio was estimated according to FINEMAN and ROSS <sup>6)</sup> and by the curve-fitting method. The  $Q_1$ ,  $e_1$  values for methyl  $\alpha$ -cyanoacrylate were then calculated by assuming that  $Q_2 = 0.74$  and  $e_2 = 0.4$  for methyl methacrylate.

### Results and Discussion

The copolymerization results are shown in Table 1.

Since no anionic homopolymerization of methyl  $\alpha$ -cyanoacrylate occurred in the presence of acetic acid, these copolymerizations were considered to proceed *via* free radical mechanism. This conclusion was also

Table 1. Copolymerization of methyl  $\alpha$ -cyanoacrylate ( $M_1$ ) with methyl methacrylate ( $M_2$ ) initiated by AIBN at 60°C in the presence of acetic acid:  $[AIBN] = 1.8 \cdot 10^{-3}$  mole/l,  $[AcOH]/[M_1] = 6.1 \cdot 10^{-2}$  in molar ratio

$[M_1]$ in comonomer (mole-%)	Time (min)	Con-version (%)	$[M_1]$ in copolymer (mole-%)	$[M_1]$ in comonomer (mole-%)	Time (min)	Con-version (%)	$[M_1]$ in copolymer (mole-%)
100.00	35	3.5	100.00	61.51	15	2.1	54.46
93.48	15	2.1	74.86	51.21	50	2.8	53.99
86.36	15	2.2	63.91	40.69	20	4.3	50.62
78.91	15	2.6	60.23	28.59	20	3.8	46.94
70.59	15	2.3	59.20	14.32	35	3.9	39.97

confirmed from the fact that the fractionated copolymer fractions were of similar composition. From Table 1, the rates of copolymerization were found to decrease slightly with increasing concentration of cyanoacrylate in the monomer mixture.

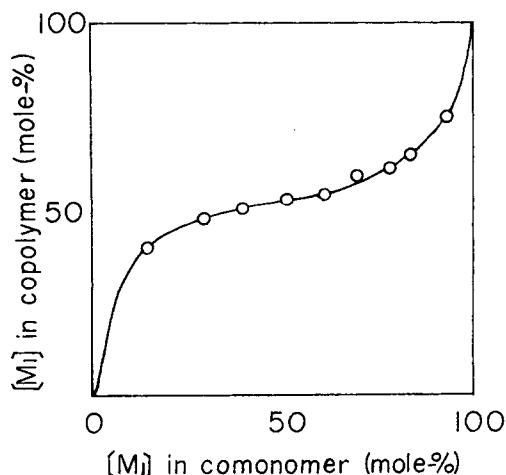


Fig. 1. Monomer-copolymer composition curve for radical copolymerisation of methyl  $\alpha$ -cyanoacrylate ( $M_1$ ) with methyl methacrylate ( $M_2$ ) at 60°C

Fig. 1 shows the monomer-copolymer composition curve. From this figure, it is noted that these monomer pairs show high tendency for alternating copolymerization. Similar behavior was also observed for the copolymerization of alkyl  $\alpha$ -phenylacrylate with styrene<sup>4,7</sup>. Monomer reactivity ratios and  $Q$ ,  $e$  values for methyl  $\alpha$ -cyanoacrylate are shown in Table 2, in which those reported for some  $\alpha$ -substituted acrylate monomers are also indicated.

Table 2. Copolymerization parameters for methyl  $\alpha$ -substituted acrylate ( $M_1$ ) and methyl methacrylate ( $M_2$ ) at 60°C

$\alpha$ -Substituents	$r_1$	$r_2$	$1/r_2$	$Q_1$	$e_1$
CN	0.13	0.10	10.0	17	2.48
Cl <sup>a)</sup>	2.00	0.15	6.67	7.7	1.50
Br <sup>a)</sup>	2.08	0.23	4.35	4.5	1.25
C <sub>6</sub> H <sub>5</sub> <sup>b)</sup>	$0 \pm 0.03$	$0.3 \pm 0.1$	3.33	6.1	1.3

<sup>a)</sup> Data of BEVINGTON *et al.*<sup>8)</sup>. <sup>b)</sup> Data of TSURUTA *et al.*<sup>4)</sup> at 65°C.

As is shown in this table, the relative reactivities ( $1/r_2$ ) of these  $\alpha$ -substituted acrylate monomers towards the poly(methyl methacrylate) radical were found to increase regularly with an increase of electron-attracting nature of the  $\alpha$ -substituents as in the case of the effect of the ester alkyl substituents in alkyl acrylates<sup>3)</sup> and methacrylates<sup>1)</sup>. It is interesting to note that the reported  $Q$  values for  $\alpha$ -substituted acrylate monomers except those having  $\alpha$ -alkyl substituents<sup>4)</sup> are larger than unity, and the  $Q$  and  $e$  values for methyl  $\alpha$ -cyanoacrylate are quite comparable with those for vinylidene cyanide ( $Q = 20.13$ ,  $e = 2.58$ )<sup>9)</sup>.

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<sup>1)</sup> T. OTSU, T. ITO, and M. IMOTO, J. Polymer Sci. B **3** (1965) 113.

<sup>2)</sup> T. OTSU, T. ITO, and M. IMOTO, J. Polymer Sci. Part A-1, **4** (1966) 733.

<sup>3)</sup> T. OTSU, T. ITO, T. FUKUMIZU, and M. IMOTO, Bull. chem. Soc. Japan **39** (1966) 2257.

<sup>4)</sup> K. CHIKANISHI and T. TSURUTA, Makromolekulare Chem. **73** (1964) 231.

<sup>5)</sup> G. G. CAMERON and G. P. KERR, European Polymer J. **3** (1967) 1.

<sup>6)</sup> M. FINEMAN and S. D. ROSS, J. Polymer Sci. **5** (1950) 269.

<sup>7)</sup> T. OTSU, B. YAMADA and T. NOZAKI, J. chem. Soc. Japan, ind. Chem. Sect. [Kōgyō Kagaku Zasshi] **70** (1967) 1941.

<sup>8)</sup> J. C. BEVINGTON, D. O. HARRIS, and M. JOHNSON, European Polymer J. **1** (1965) 235.

<sup>9)</sup> Cf. L. J. YOUNG, Copolymerization, Ed. G. E. HAM, Interscience Publ., New York 1964, p. 845.