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Bulk Copolymerization of Acrylonitrile with α-Chloroacrylonitrile

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Synopsis. Copolymerization of acrylonitrile (M_1) with α-chloroacrylonitrile (M_2) was carried out at 60 °C using 4.3×10^{-2} mol% of α,α′-azobisisobutyronitrile. The four copolymers obtained were analyzed, their mole fractions of α-chloroacrylonitrile units being 0.196, 0.377, 0.532, and 0.722, and the monomer reactivity ratios r_1 and r_2 were found to be 0.31 and 3.25, respectively.

Copolymerization of acrylonitrile (M_1) with α-chloroacrylonitrile (CAN (M_2)) was carried out in order to obtain model compounds of chlorinated polyacrylonitrile. The monomer reactivity ratios r_1 and r_2 were evaluated by the Mayo-Lewis method.[1] So far the values have been reported only once.[2]

Experimental

Preparation of Copolymers. Commercial acrylonitrile and CAN were distilled in nitrogen atmosphere and then kept in a refrigerator. Both monomers were charged in the amounts given in Table 1 in the reaction vessel which was alternately evacuated with an oil pump and flushed with nitrogen. The bulk copolymerization was carried out at 60 °C in the presence of 4.3×10^{-2} mol% of α,α′-azobisisobutyronitrile (AIBN). The reaction vessel was sealed in order to prevent the loss of both monomers during the course of copolymerization, the reaction system being stirred magnetically. After the lapse of the required reaction time, hydroquinone was added in an amount equivalent to AIBN in order to terminate copolymerization. Copolymer was filtered, washed thoroughly with methanol, and finally dried in a vacuum at 30 °C to constant weight.

Chlorine Analysis. The method was reported in a previous work.[3]

Results and Discussion

The analytical data of products are summarized in Table 1. The mole fraction of CAN units in each copolymer was calculated by means of chlorine content. Figure 1 shows the relationship between the mole fraction obtained and that of CAN in monomer mixture at the start of reaction. Since the monomer concentrations, $[M_1]$ and $[M_2]$, at the time when polymerization ceased can be determined by means of the yield and the composition of copolymer, the lines on r_1-r_2 plots are obtained by means of Mayo-Lewis's integrated equation.[1] The lines have a common intersection near $r_1=0.31$, $r_2=3.25$, except for Experiments 6 and 7 in which light brown and brown products, respectively, were obtained. Coloration of the products in Experiments 2—5 was very faint. A side reaction would proceed simultaneously with copolymerization, being enhanced when the initial mole fraction of CAN is over 0.5.

Table 1. Copolymerization of acrylonitrile with CAN by AIBN at 60 °C

Expt No.	Reaction conditions			Analytical data of product	
	Acrylonitrile (M_1) g	CAN (M_2) g	Time h	Yield wt%	Chlorine content wt%
1	20.15	0	0.25	4.7	0
2	18.13	2.75	10	22.0	11.60
3	16.12	5.39	24	9.7	20.25
4	14.10	8.25	48	4.8	26.40
5	10.07	13.76	19	2.9	32.85
6	8.06	16.51	24	4.3	33.45
7	4.03	22.02	24	4.6	33.37

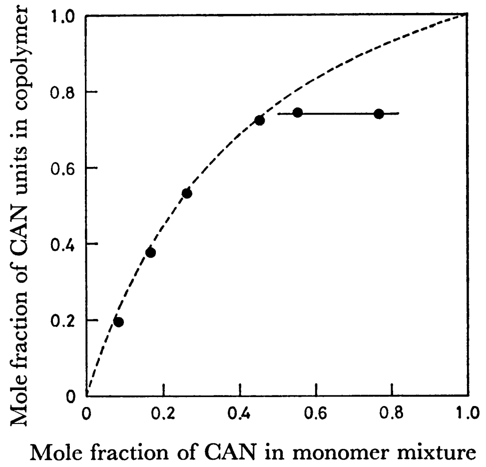

Fig. 1. Composition of copolymers.
A broken line is the initial copolymer composition curve for $r_1=0.31$, $r_2=3.25$.

In copolymers obtained in Experiments 2, 3, 4, and 5, the mole fractions of CAN units were 0.196, 0.377, 0.532, and 0.722, respectively. It seems that CAN units are distributed at random in the copolymer chain, since the reactivity ratio product (r_1r_2) is approximately equal to unity.

References

1) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

2) "Vinyl and Diene Monomers, Part 1," ed by E. C. Leonard, John Wiley & Sons, Inc., New York (1970), p. 65.

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