The Reactivity Ratios of Long-Chain Acrylic Esters

The literature on vinyl polymerization contains several references[1] to the influences on reactivity ratios by the alkyl group in an ester of an α,β-unsaturated acid and the acyl group in a vinyl ester. It has been shown in these discussions that the size of the alkyl group as well as that of the acyl group does not greatly influence the reactivity ratios of such esters in copolymerizations with other monomers. We have now found that the two long-chain alkyl esters of acrylic acid, dodecyl acrylate and octadecyl acrylate, do not give the same reactivity ratios with acrylonitrile as had been determined for methyl acrylate.

Dodecyl acrylate was prepared essentially by the method of Rehberg and Fisher,[2] except that the product was extracted with alkali prior to fractional distillation. Purification by distillation only failed because the sublimation of hydroquinone as an inhibitor occurred through the operation (b.p. 120° at 1 mm., n_D^{20} 1.4440, saponification eq., calcd. 240.4; found 238.5).

Octadecyl acrylate monomer was prepared in the same manner as dodecyl acrylate and isolated from hydroquinone by the manner of Jordan et al.[3] (m.p. 31°, saponification eq., calcd. 324.5; found 325.1).

Other monomers were commercial materials, distilled before use and stored in an icebox (methyl acrylate, b.p. 80°, n_D^{20} 1.4040: butyl acrylate, b.p. 39° at 10 mm., n_D^{20} 1.4190: acrylonitrile, b.p. 77°, n_D^{25} 1.3888).

Bulk copolymerization was carried out in a 50-ml. Pyrex tube using 2, 2'-azobisisobutyronitrile as an initiator at 60°. The conversion was kept below 10%, and a wide range of monomer mixture was used in order to minimize the errors arising from changes in the monomer composition. All emulsion copolymerizations utilized 20 g. of total monomers, 0.05 g. of potassium persulfate as an initiator, and 100 ml. of the emulsifier
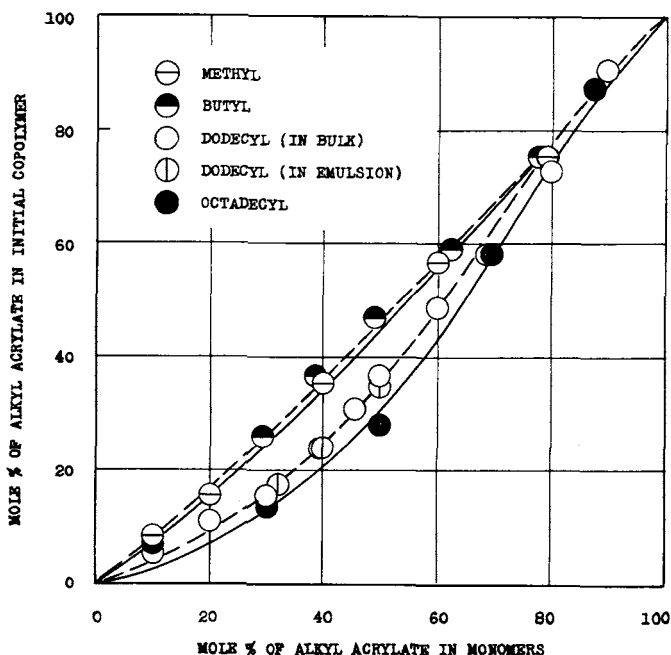

Fig. 1. Monomer-copolymer composition curves for methyl acrylate, butyl acrylate dodecyl acrylate, and octadecyl acrylate with acrylonitrile.

solution which was prepared by dissolving 5 g. of sodium lauryl sulfate in 1000 ml. of distilled water.   The reaction mixture was stirred for one hour at room temperature and polymerized at 60° under stirring and bubbling with oxygen-free nitrogen.   In the both cases, the initial copolymers were isolated by pouring the entire reaction mixtures into stirred methanol, purified by reprecipitations, and the amounts of combined acrylonitrile were determined by duplicate Kjeldahl analyses.   In the case of octadecyl acrylate copolymer, a methanol extraction with a Soxhlet's extractor was used for removing the unreacted acrylate and two reprecipitations.

TABLE I

Azobisnitrile-Catalyzed Bulk Copolymerization of Alkyl Acrylates with Acrylonitrile at 60°[a]

Mole-%, in monomer mixture	Nitrogen analyses, %[b]	Calcd. mole-% of acrylate in copolymer
Methyl acrylate		
10.01	23.1	8.1
20.18	20.3	15.6
39.82	14.1	35.0
60.30	8.43	56.8
79.35	4.45	75.2
Butyl acrylate		
29.42	14.3	25.9
38.90	11.0	36.7
49.09	8.41	46.9
62.48	5.85	59.2
78.86	3.16	75.3
Dodecyl acrylate		
10.03	20.9	5.5
19.99	17.0	10.9
30.04	14.5	15.3
39.83	10.9	23.9
45.21	8.83	30.5
50.18	7.29	36.7
59.84	5.00	48.6
68.81	3.66	57.8
79.95[c]	2.00	72.9
89.98[c]	0.602	90.4
31.80[d]	13.5	17.5
39.75[d]	10.9	23.9
49.99[d]	7.74	34.7
Octadecyl acrylate		
10.04	18.6	6.4
30.02[e]	13.8	13.0
49.88[e]	7.72	28.3
69.52[e]	2.82	57.8
87.46[e]	0.631	87.0

[a] The reprecipitation solvent was dimethyl formamide, except for those noted in the table, and the nonsolvent was methanol.

[b] Duplicate values obtained were meaned and corrected for the experimental value of 25.55% N in polyacrylonitrile.

[c] Solvent, benzene.

[d] The copolymerization was carried out in emulsion.

[e] Solvent, petroleum ether.

The results of the investigation are summarized in Table I from which the monomer-copolymer composition curves (Fig. 1) for the four series of experiments were drawn.

From Figure 1 it will be seen that the monomer-copolymer composition curves for the two series of methyl acrylate and butyl acrylate are identical within analytical error. It will be also observed that the copolymers of dodecyl acrylate and octadecyl acrylate contain more combined acrylonitrile than the corresponding copolymer of methyl acrylate. In determining the monomer reactivity ratios for acrylic esters and acrylonitrile, the method of Fineman and Ross[4] was used, since only products obtained at low conversions were analyzed. The reactivity ratios for methyl acrylate and acrylonitrile have been determined by Okamura and Yamashita[5] and by Marvel and Schwen.[1] We have also determined these values under the same conditions used for the long-chain alkyl acrylates, and report our results in Table II.

TABLE II
Monomer Reactivity Ratios for Alkyl Acrylates with Acrylonitrile

Acrylates	r_1 (nitrile)	r_2 (ester)
Methyl	1.4 ± 0.1	0.95 ± 0.05
Butyl	1.2 ± 0.1	0.89 ± 0.08
Dodecyl	3.2 ± 0.5	1.3 ± 0.1
Octadecyl	4.1 ± 0.8	1.2 ± 0.1

Our values for methyl acrylate and acrylonitrile are quite close to those reported.

As complementary evidence to show the difference in reactivity between the short chain acrylate and long chain one, the variation curves of the average copolyer composition vs. the degree of conversion are shown in Figure 2. The curves were drawn from the data in Table III.
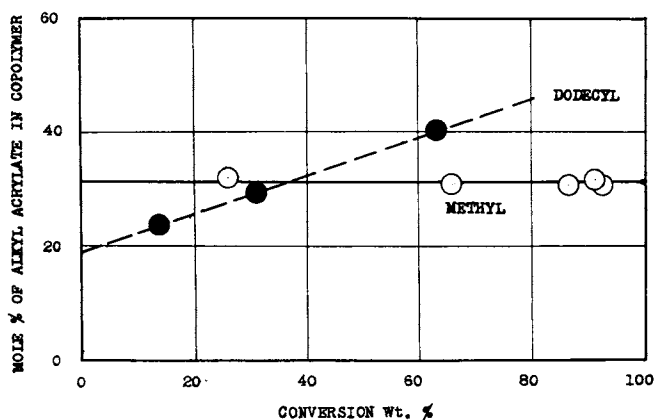

Fig. 2. Variations of the average composition with the conversion of methyl acrylate-acrylonitrile copolymer and dodecyl acrylate-acrylonitrile copolymer.

In the case where both r_1 and r_2 are about 1, the average copolymer composition does not change at any conversion, while in the case where $r_1 > r_2$, the average content of acrylate in the copolymer clearly changes with the degree of conversion. In the experiment for Figure 2, an emulsion technique was used instead of bulk one because of the ease of conversion control. There may be some question about such a treatment. A few points for the emulsion copolymerization of acrylonitrile and dodecyl acrylate are also plotted in Figure 1, and from this it will be observed that the emulsion curve lies

TABLE III

Variation of the Average Composition with the Conversion of Alkyl Acrylate-Acrylonitrile Copolymer

Conversion, wt.-%	Nitrogen analyses, %[a]	Calcd. mole-% in copolymer
		Methyl acrylate
25.7[b]	15.0	31.9
65.9	15.3	30.9
86.9	15.3	30.9
91.1	15.2	31.2
92.5	15.4	30.6
		Dodecyl acrylate
13.8[c]	10.9	23.9
13.8	10.9	23.9
31.0	9.27	29.0
63.4	6.38	40.9

[a] Duplicate values obtained were meaned and corrected.

[b] This series of experiments was started from a 31:69 (mole-%) methyl acrylate-acrylonitrile monomer mixture in emulsion.

[c] Started from a 40:60 dodecyl acrylate-acrylonitrile in emulsion.

very close to the bulk one. The same results have been given by Uchida and Nagao[6] and by Marvel and Schwen[1] for acrylonitrile and methyl acrylate. From the above considerations it seems possible to discuss bulk and emulsion copolymerization without any distinction in this particular case.

On the basis of these data, it seems reasonable to assume that the reactivity of the acrylic acid portion of the ester in copolymerization is influenced by the long-chain alkyl groups, such as dodecyl or octadecyl, in the ester.

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