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Polymerizable Derivatives of Long-Chain Alcohols. II. Reactivity Ratios for the Copolymerization of Some Alkyl Acrylates*†

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A considerable number of authors have demonstrated that neither the length of the acyl group in vinyl esters[2] nor the length of the alkyl group in esters of α,β-unsaturated acids[3] influences appreciably the magnitude of the monomer reactivity ratios in the free radial copolymerization of these monomers. The products of r_1 and r_2 are either one or less than one in conformance with the empirical generalization[4] that a product of one cannot be exceeded.

Cameron et al.[6] plotted the reciprocal of r_1 against alkyl chain length for a series of methacrylate esters (M_1) copolymerizing with methacrylonitrile and found a peak occurring at the propyl ester. Tamikado and Iwakura,[7] reporting the monomer reactivity ratios for several alkyl acrylates and acrylonitrile, found a drift in the values of r_1 and r_2 which increased with increasing alkyl chain length. The products of r_1 and r_2 were considerably greater than one. The drift observed by Tamikado and Iwakura prompted the present determination of the monomer reactivity ratios for three normal alkyl (butyl, octyl, and octadecyl) acrylates and, respectively, acrylonitrile and vinylidene chloride.

TABLE I
Monomer Reactivity Ratios. Alkyl Acrylates and Acrylonitrile

Acrylate (M_2)	Present work			Literature values		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
Methyl				1.5 ± 0.1[a]	0.84 ± 0.05[a]	1.26
				0.83[b]	0.84[b]	0.70
				1.4 ± 0.1[c]	0.95 ± 0.05[c]	1.33
Butyl	1.52 ± 0.03	0.75 ± 0.18	1.14	1.2 ± 0.1[c]	0.89 ± 0.08[c]	1.07
Octyl	1.93 ± 0.08	0.83 ± 0.23	1.60			
Dodecyl				3.2 ± 0.5[c]	1.3 ± 0.1[c]	4.16
Octadecyl	1.74 ± 0.04	0.68 ± 0.18	1.18	4.1 ± 0.8[c]	1.2 ± 0.1[c]	4.92
Composite	1.61 ± 0.04	0.50 ± 0.19	0.80			

[a] Data of Marvel and Schwen.[3c]
[b] Data of Okamura and Yamashita.[8]
[c] Data of Tamikado and Iwakura.[7]

In several recent papers, however, regular and irregular drifts have been reported in the values of r_1 and r_2 with change in the length of the alkyl group in acrylate and methacrylate comonomers. The list of monomer reactivity ratios for the copolymerization of alkyl methacrylates and vinyl acetate reported recently by Szo-Kwei Min and Chen-Ho Chu[5] showed a set of values with methyl methacrylate lower than those for the other methacrylate esters reported; the product r_1r_2 was much greater than one in all cases except for the methyl ester.

RESULTS AND DISCUSSION

The monomer reactivity ratios found for the copolymerization of alkyl acrylates and acrylonitrile are listed in Table I. As can be seen, no regular drift was found in the values of r_1 and r_2 with variation in the chain length of the alkyl radical, and, in fact, the values changed very little. The previously reported results of Marvel and Schwen,[3c] of Okamura and Yamashita,[8] and of Tamikado and

* For part I of this series, see ref. 1.

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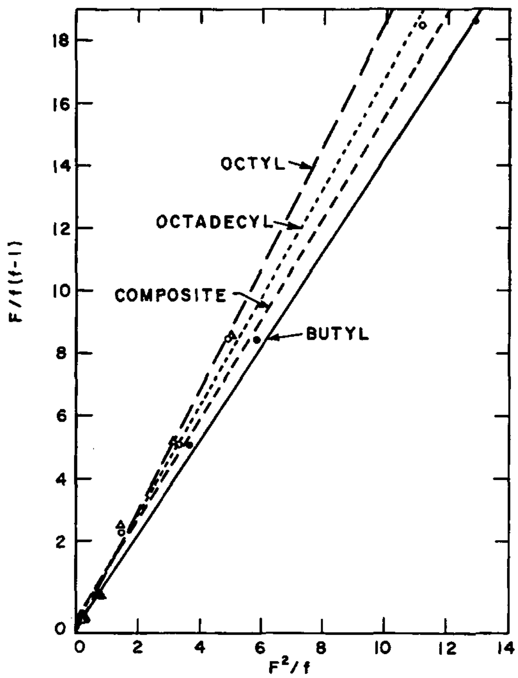

Fig. 1. Copolymerization of acrylonitrile and alkyl acrylates.

Iwakura[7] are also listed in Table I. The contrast of the data reported by the latter authors with those presented in this paper is obvious.

From the presently reported data, if it is assumed that the alkyl chain length has *no* effect on the kinetic constants, new values for the monomer reactivity ratios may be calculated for the copolymerization of the generalized alkyl acrylate and acrylonitrile. The Fineman and Ross[9] parameters used in the determination of the monomer reactivity ratios for each alkyl acrylate (butyl, octyl, and octadecyl) were all used to compute, by the least squares method, a single line best fitting the data. The slope and the negative of the intercept of this line gave, respectively, r_1 and r_2 for acrylonitrile and the composite alkyl acrylate (Table I). The validity of calculating composite values of r_1 and r_2 does not rest entirely on an assumption of a generalized alkyl acrylate. In Table I the deviations in the values of the monomer reactivity ratios for the composite alkyl acrylates are of the same order of magnitude as those for the individual ratios. It may be inferred, therefore, that it is of no greater validity to assume that the points computed for each monomer pair from the Fineman and Ross parameters belong to the statistical population defining the individual lines than it is to assume that the points represent the population of the composite line. It may be significant, too, that whereas the composite r_1r_2 product is less than one, the individual r_1r_2 products are each greater than one. A graphical representation of the Fineman and Ross parameters for the copolymerization of alkyl acrylates and acrylonitrile is shown in Figure 1.

TABLE II
Monomer Reactivity Ratios.
Alkyl Acrylates and Vinylidene Chloride

Acrylate (M_2)	r_1	r_2
Methyl	1[a]	1[a]
Butyl	0.88 ± 0.10	0.83 ± 0.02
Octyl	0.87 ± 0.02	0.70 ± 0.01
Octadecyl	0.91 ± 0.05	1.01 ± 0.01
Composite	0.88 ± 0.04	0.84 ± 0.01

[a] Data of Mayo et al.[10]

The monomer reactivity ratios for the copolymerization of the alkyl acrylates chosen and vinylidene chloride are shown in Table II. In this system too, no drift in the values of the monomer reactivity ratios was found when the alkyl chain length was varied. A composite value was again calculated from the present experimental data as shown

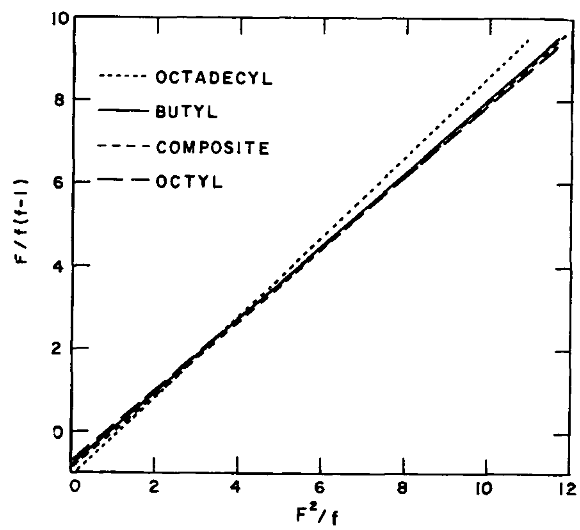

Fig. 2. Copolymerization of vinylidene chloride and alkyl acrylates.

in Table II. There is fair agreement with values for methyl acrylate and vinylidene chloride cited from the work of Mayo et al.[10] In the graphical representation of the parameters and the least-squares lines shown in Figure 2, the individual points were omitted to avoid confusion.

EXPERIMENTAL

Reagents

Octadecyl acrylate was prepared by the method of Jordan et al.,[1] m.p. 31.5–32.5°C., saponification number, calculated 172.9, found 172.4, n_D^{35} 1.4460. Octyl acrylate was a commercial grade which was purified by the method of Riddle,[11] saponification number calculated 304.9, found 301.4. Butyl acrylate was a purified[11] commercial grade, saponification numbeı calculated, 438.0 found, 434.1. Acrylonitrile, b.p. 77–77.5°C., n_D^{25} 1.3888 was obtained by distilling a commercial grade through a 1-ft. Widmer column. Vinylidene chloride, b.p. 31.0–32.0°C., was distilled through a 1-ft. Widmer column from the commercial grade immediately before use. *tert*-Butyl alcohol was distilled through a 2-ft. Vigreux column, and the fraction boiling at 81.5–81.7°C., melting at 25.0–25.5°C. was used. The methanol used was ACS grade.

Copolymerization of Alkyl Acrylates and Acrylonitrile

Copolymerization was conducted in *tert*-butanol at 60°C. A solution method was used to prevent the large increase in branching known to occur when acrylonitrile polymerizes in bulk. *tert*-Butanol was selected because it transfers only to a small extent[12] with acrylonitrile ($C_s = 0.44 \times 10^{-4}$), and thus analytical errors caused by solvent fragments in the polymer chains were minimized. The total weight of monomers used was 15 g. The alkyl acrylate and the acrylonitrile were weighed successively with analytical precision into a glass-stoppered flask under a nitrogen atmosphere. This solution was transferred quickly with the aid of *tert*-butanol (4 moles/mole of total monomers) to glass-stoppered cylinders. Benzoyl peroxide was used as the initiator (0.2 mole-% based on monomers for the octadecyl acrylate series, 0.1 mole-% for the butyl and octyl acrylate series). To remove oxygen, the mixture was chilled to −80°C., evacuated at 20 mm., and flushed with nitrogen, and the freezing and flushing process was repeated. The solutions were then heated in a bath kept at 60 ± 0.1°C. The copolymers were isolated by precipitation into methanol (3 volumes per volume of reagents) and were extracted free from monomers by several 2-hr. hot methanol extractions. The ground polymers were dried to constant weight in a circulating oven at 50°C. for two days. The compositions of the copolymers were calculated from their nitrogen contents which were determined by the Kjeldahl method and were confirmed, in some cases, by the Dumas procedure. No correction was needed for the Kjeldahl method because the theoretical nitrogen content was found for polyacrylonitrile provided fresh sulfuric acid was used. The experimental data for the copolymerization are given in Table III. The Fineman and Ross procedure was used to determine the monomer reactivity ratios and Birge's[13] method was used to compute the least squares slope and intercept and their deviations.

TABLE III
Copolymerization of Acrylonitrile (M_1) and Alkyl Acrylates (M_2)

Acrylate	Sample no.	Conversion, %	M_2	Nitrogen, %	m_2
Butyl	1	3.8	0.0494	24.35	0.0335
	2	2.4	0.0992	22.59	0.0655
	3	2.1	0.1494	20.80	0.1004
	4	2.5	0.4991	9.42	0.4280
	5	4.5	0.7494	3.48	0.7318
Octyl	1	3.6	0.0997	21.86	0.0566
	2	5.7	0.1503	19.80	0.0879
	3	11.8	0.2500	16.99	0.1372
	4	8.0	0.5007	6.88	0.4496
	5	13.2	0.7532	3.19	0.6769
Octadecyl	1	13.9	0.0499	22.31	0.0298
	2	13.0	0.1003	19.33	0.0571
	3	15.0	0.1502	16.29	0.0927
	4	18.9	0.2636	12.34	0.1576
	5	8.1	0.5013	4.60	0.4369
	6	27.3	0.7542	1.57	0.7212

Copolymerization of Alkyl Acrylates and Vinylidene Chloride

Benzoyl peroxide (0.25 mole-% for the octadecyl acrylate copolymers, 0.1 mole-% for the other copolymers), the alkyl acrylate and vinylidene chloride were weighed in successive order with analytical precision into tubes which were sealed and heated at 50 ± 0.1°C. The copolymers were isolated and purified by the same procedure used for the acrylonitrile copolymers. The composition of the copolymers were calculated from their chlorine contents which were determined by the Carius combustion method and were checked by a modified Schöniger procedure.[14] In Table IV the experimental data which were used in computation of the monomer reactivity ratios are given.

TABLE IV
Copolymerization of Vinylidene Chloride (M_1) and Alkyl Acrylates (M_2)

Acrylate	Sample No.	Conversion, %	M_2	Chlorine, %	m_2
Butyl	1	1.2	0.0966	62.57	0.1093
	2	2.3	0.1094	62.13	0.1142
	3	4.5	0.2461	50.66	0.2478
	4	5.2	0.3841	39.79	0.3850
	5	6.6	0.4989	37.91	0.4917
	6	7.5	0.6187	24.04	0.6050
	7	7.2	0.7187	17.61	0.7030
Octyl	1	2.3	0.1245	56.12	0.1346
	2	4.2	0.2459	44.60	0.2491
	3	5.4	0.3612	35.18	0.3595
	4	5.9	0.4895	26.69	0.4757
	5	4.7	0.6168	20.14	0.5786
	6	4.6	0.6989	16.19	0.6475
Octadecyl	1	4.4	0.1220	48.20	0.1319
	2	4.0	0.2451	33.95	0.2544
	3	3.0	0.3600	23.14	0.3903
	4	1.1	0.4827	17.17	0.4915
	5	0.7	0.6041	12.05	0.6007
	6	1.2	0.7225	7.03	0.7363

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Synopsis

Monomer reactivity ratios were determined for the copolymerization of some alkyl acrylate esters and, respectively, acrylonitrile and vinylidene chloride. For acrylonitrile (M_1), the values found were: for butyl acrylate, r_1 = 1.52 ± 0.03, r_2 = 0.75 ± 0.18; for octyl acrylate, r_1 = 1.93 ± 0.08, r_2 = 0.83 ± 0.23; for octadecyl acrylate, r_1 = 1.74 ± 0.04, r_2 = 0.68 ± 0.18. If it is assumed that there is no change in the magnitude of the kinetic constants with chain length, a value for the generalized alkyl acrylate and acrylonitrile may be calculated and r_1 = 1.61 ± 0.04, r_2 = 0.50 ± 0.19. Values found with vinylidene chloride (M_1) were: for butyl acrylate, r_1 = 0.88 ± 0.10, r_2 = 0.83 ± 0.02; for octyl acrylate, r_1 = 0.87 ± 0.02, r_2 = 0.70 ± 0.01; for octadecyl acrylate, r_1 = 0.91 ± 0.05, r_2 = 1.01 ± 0.01. For the generalized alkyl acrylate, the calculated values were r_1 = 0.88 ± 0.04, r_2 = 0.84 ± 0.01.

Résumé

Les rapports de réactivité ont été déterminés au cours dela copolymérisation de quelques acrylates d'alcoyle avec, respectivement, l'acrylonitrile et le chlorure de vinylidéne. Pour l'acrylonitrile (M_1) les valeurs trouvées sont: r_1 = 1,52 ± 0,03 et r_2 = 0,75 ± 0,18 pour l'acrylate de butyle; r_1 = 1,93 ± 0,08 et r_2 = 0,83 ± 0,23 pour l'acrylate d'octyle; et r_1 = 1,74 ± 0,04 et r_2 = 0,68 ± 0,18 pour l'acrylate d'octadécyle. Si l'on admet que les constantes cinétiques ne varient pas avec la longueur de la chaine, on peut calcular une valeur généralisée pour les acrylates d'alcoyle et l'acrylonitrile; dans ce cas r_1 = 1,61 ± 0,04 et r_2 = 0,50 ± 0,19. Les valeurs trouvées pour le chlorure de vinylidène (M_1) sont: r_1 = 0,88 ± 0,1 et r_2 = 0,83 ± 0,02 pour l'acrylate de butyle; r_1 = 0,87 ± 0,02 et r_2 = 0,7 ± 0,01 pour l'acrylate d'octyle; r_1 = 0,91 ± 0,05 et r_2 = 1,01 ± 0,01 pour l'acrylate d'octadécycle. Les valeurs généralisées pour les acrylates d'alcoyles sont r_1 = 0,88 ± 0,04 et r_2 = 0,84 ± 0,01.

Zusammenfassung

Für die Copolymerisation einiger Acrylsäurealkylester mit Acrylnitril bzw. Vinylidenchlorid wurden die Monomerreaktivitätsverhältnisse bestimmt. Bei Acrylnitril (M_1) betrugen die gefundenen Werte: für Butylacrylat r_1 = 1,52 ± 0,03 und r_2 = 0,75 ± 0,18; für Octylacrylat r_1 = 1,93 ± 0,08 und r_2 = 0,83 ± 0,23; für Octadecylacrylat r_1 = 1,74 ± 0,04 und r_2 = 0,63 ± 0,18. Unter der Annahme, dass die Grösse der kinetischen Konstanten nicht von der Kettenlänge abhängt, können für Alkylacrylate und Acrylnitril die Durchschnittswerte r_1 = 1,61 ± 0,04 und r_2 = 0,50 ± 0,19 angegeben werden. Bei Vinylidenchlorid (M_1) betrugen die gefundenen Werte: für Butylacrylat r_1 = 0,88 ± 0,10 und r_2 = 0,83 ± 0,02; für Octylacrylat r_1 = 0,87 ± 0,02 und r_2 = 0,70 ± 0,01; für Octadecylacrylat r_1 = 0,91 ± 0,05 und r_2 = 1,01 ± 0,01. Die Durchschnittswerte für Alkylacrylat betrugen r_1 = 0,88 ± 0,04 und r_2 = 0,84 ± 0,01.

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