

Reactivity Ratios and Copolymerization Parameters for Copolymers Incorporating *n*-Octadecyl Acrylate and *N*-*n*-Octadecylacrylamide

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Synopsis

Monomer reactivity ratios and copolymerization parameters were determined for *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide with several monomers not previously reported. Values of Q and e for the long-chain acrylate now agreed more closely than before with the average of values for the lower acrylate homologs. The average polarity parameter for *N*-*n*-octadecylacrylamide still showed more electron withdrawal from the double bond ($e = 0.42$) than was expressed by the average literature value ($e = -0.10$) for *N*-*n*-octylacrylamide. Because penultimate effects were absent in this work, the reason for the discrepancy seems to reside in the copolymer analysis. Reactivity ratios for oleyl and octadecyl acrylate with methyl methacrylate were similar. Coefficients for the relation between overall rates of copolymerization and composition were obtained on some systems by curve fitting with a computer. They generally showed a slight minimum.

It is generally accepted that homologous series of vinyl monomers with linear side chains exhibit similar reactivity in copolymerization¹ and therefore have proximate Q and e parameters.² As published lists of Q and e values reveal,³ similar reactivity is found for broad classes of vinyl monomers, including vinyl esters, ethers, 1-alkenes, *n*-alkyl acrylates, methacrylates, *N*-*n*-alkylacrylamides, and methacrylamides. Although especially refined techniques, involving use of labeled monomers, have demonstrated recently that small drifts in reactivity occur with side-chain length,⁴ these techniques have not been widely applied so far. Apparent deviations for individual vinyl homologs exist, however, in the published compilations. Discrepancies were found, for example, in the values of Q and e for *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide which are monomers of concern to this laboratory. Values for *n*-octadecyl acrylate ($Q = 0.42$, $e = 1.12$),³ compared with an average value for the shorter *n*-alkyl acrylates ($Q = 0.44 \pm 0.06$, $e = 0.67 \pm 0.32$)³ showed a discrepancy in the polarity parameter e . Values found for *N*-*n*-octadecylacrylamide, reported from this laboratory,⁵ ($Q = 0.66$, $e = 1.13$), conflict even more seriously with

those reported⁶ for *N-n*-octylacrylamide ($Q = 0.18$, $e = -0.10$). *N-n*-Octadecylacrylamide had been copolymerized under conditions causing copolymer precipitation, because acrylonitrile and vinylidene chloride were two of the three comonomers employed, and *tert*-butanol was the solvent medium. While heterogeneity caused by the reaction medium should not affect the results,^{7a} a recent examination by light scattering⁸ has revealed that examples of these two copolymer systems, polymerized to high conversion, showed marked compositional drift in the nitrile copolymer but the expected drift in the vinylidene chloride system. Although cognizance was taken of the special problems found in the copolymerization of acrylonitrile,⁹ these results were still troubling. Accordingly, the present investigation of reactivity ratios was undertaken to obtain Q and e values that might more realistically apply to the long side-chain comonomers.

n-Octadecyl acrylate was copolymerized at 60°C with several comonomers not previously reported, both under heterogeneous conditions (styrene in *tert*-butanol, acrylonitrile in benzene) and homogeneously (the remainder). In addition, both the saturated C_{18} side-chain acrylate and oleyl acrylate were copolymerized with methyl methacrylate. Results, listed in Table I, show somewhat similar Q and e parameters for all, the average values now agreeing more closely with the average values for the shorter side-chain homologs. Within the deviations found in published values³ these parameters were insensitive to the effect of heterophase copolymerization and the nature of the alkyl group.

N-n-Octadecylacrylamide was copolymerized with the same two comonomers used by Bork et al.⁶ with *N-n*-octylacrylamide. Values of Q (Table I) were now similar to those found by Bork, but the value of e still indicated marked electron withdrawal from the double bond. Bork found specifically with methyl methacrylate $Q = 0.17$, $e = -0.17$, and with styrene $Q = 0.19$, $e = -0.02$.

These differences could conceivably be caused by penultimate amide groups¹⁰ acting to retard amide addition, the effect being more apparent in the limits of a low M_1/M_2 ratio. The longer side chains in the C_{18} amide might exhibit this effect to a greater extent than the shorter-chain comonomers, although the available data^{1,9} do not lend support to this idea. Nevertheless, the data for the two amide systems, as well as those for octadecyl and oleyl acrylate with methyl methacrylate and octadecyl acrylate with acrylonitrile, were tested for penultimate effects at both extremes of the feed ratios. Methods used were those of Barb¹⁰ and Ham,¹¹ together with the more recent treatments of Hecht¹² and Guyot and Guillot.¹³ The last method is convenient when both r_1 and r_2 are significantly large, as in the present cases. No evidence was found for a penultimate effect by any treatment. On the other hand, the copolymer composition-feed data were well fitted by the reactivity ratios of Table I, especially in those cases (Tables II, III) where many observations were made.

The disturbingly large and unlikely¹⁴ $r_1 r_2$ product ($r_1 r_2 = 1.7$) found for the *N-n*-octadecylacrylamide-methyl methacrylate system was thought to

TABLE I
Monomer Reactivity Ratios and Copolymerization Parameters for *n*-Octadecyl
Acrylate and *N*-*n*-Octadecylacrylamide with Various Monomers at 60°C

M ₁	M ₂	Solvent	r ₁	r ₂	Q ₂	e ₂
Styrene	<i>n</i> -Octadecyl acrylate	<i>tert</i> -Butanol	0.44 ± 0.07	0.18 ± 0.45	0.64	0.79
"	"	Benzene	0.79 ± 0.09	0.31 ± 0.31	0.49	0.39
"	"	None	0.75 ± 0.12	0.34 ± 0.06	0.52	0.37
Acrylonitrile	"	Benzene	1.61 ± 0.34	0.40 ± 0.12	0.17	0.54
Methyl meth- acrylate	"	"	2.36 ± 0.04	0.48 ± 0.12 ^b	0.33	0.50
"	Oleyl acrylate	"	2.23 ± 0.01	0.30 ± 0.03	0.43	1.03
Vinylidene ^a chloride	<i>n</i> -Octadecyl acrylate	None	0.91 ± 0.05	1.01 ± 0.01	0.27	0.65
				Avg.	0.41 ± 0.13	0.61 ± 0.18
Methyl meth- acrylate	<i>N</i> - <i>n</i> -Octadecyl- acrylamide	Benzene	3.85 ± 0.17	0.44 ± 0.04 ^c	0.26	0.50
Styrene ^d	"	"	1.41 ± 0.10	0.20 ± 0.05	0.29	0.33
				Avg.	0.28 ± 0.02	0.42 ± 0.09

^a Data of Jordan et al.¹

^b For the Q₂, e₂ parameter calculation, r₂ was set equal to 0.42.

^c For the Q₂, e₂ parameter calculation, r₁ and r₂ were fitted by an iterative procedure to the experimental copolymer composition feed curve by assuming r₁r₂ = 0.99. Reactivity ratios by this procedure were: r₁ = 3.00, r₂ = 0.33.

^d At 80°C.

TABLE II
Copolymerization of *n*-Octadecyl (or Oleyl) Acrylate (M_2) and Various Monomers (M_1)

Monomer	Solvent	Conversion, %	M_2	Analysis		Rate of copolymerization ^a R_p , mole/kg-sec $\times 10^4$	
				C, %	m_2	Found	Calcd
Styrene	<i>tert</i> -Butanol	0.48	0.1500	85.52	0.2169		
		10.11	0.1500	85.06	0.2392		
Styrene	Benzene	2.39	0.3000	84.32	0.2783		
		5.77	0.5000	82.37	0.4054		
		2.59	0.7500	78.97	0.7727		
		9.55	0.1500	86.90	0.1577		
		10.56	0.3000	83.66	0.3170		
		10.16	0.5000	83.35	0.3366		
Styrene	Bulk	10.56	0.7500	79.92	0.6424		
		13.76	0.0500	89.92	0.0579		
		14.10	0.1000	88.10	0.1138		
		12.74	0.1500	86.62	0.1689		
		13.52	0.2000	85.58	0.2141		
		9.81	0.3000	84.13	0.2891		
Acrylonitrile		10.36	0.4000	81.61	0.4674		
		6.18	0.5000	82.77	0.3759		
		3.75	0.7500	80.07	0.6243		
		4.87	0.1000	18.83 ^b	0.0617		
		6.52	0.2000	14.77 ^b	0.1141		
		9.00	0.3000	12.77 ^b	0.1486		
		6.49	0.4000	8.70 ^b	0.2496		
		7.14	0.6000	3.45 ^b	0.5210		
		6.70	0.7500	2.82 ^b	0.5775		

Methyl methacrylate	9.47	0.0514	61.22	0.0227	1.41	1.41
	9.93	0.1008	62.30	0.0444	0.93	1.28
	13.33	0.1008	62.40	0.0465	1.37	1.25
	8.13	0.1028	62.29	0.0441	1.46	1.25
	9.95	0.2003	64.37	0.0921	0.85	1.04
	11.87	0.1997	64.53	0.0962	1.02	1.04
	7.33	0.2021	65.18	0.1134	0.99	1.04
	4.05	0.3005	66.71	0.1587	0.34	—
	13.32	0.2975	66.32	0.1464	0.98	0.94
	7.12	0.3020	66.74	0.1596	0.93	0.93
	7.57	0.4021	68.79	0.2333	0.94	0.90
	5.84	0.5990	72.14	0.4020	0.84	0.95
	8.92	0.7005	73.75	0.5169	1.11	1.02
	9.02	0.8001	75.21	0.6518	1.20	—
	7.64	0.0510	61.28	0.0233	1.06	1.08
Methyl methacrylate (oleyl acrylate)	7.92	0.1004	62.48	0.0470	1.08	0.98
	7.19	0.2195	65.06	0.1072	0.71	0.78
	6.51	0.2993	66.67	0.1526	0.64	0.68
	6.33	0.4014	68.71	0.2221	0.59	0.59
	4.62	0.5990	72.20	0.3873	0.50	0.46
	4.71	0.7068	72.98	0.4360	0.44	0.42
	3.02	0.7985	75.30	0.6212	0.30	0.39
	4.69	0.8071	74.30	0.5327	0.36	0.39

^a Rates at 60°C calculated by using the coefficients of Table IV.^b Values for the acrylonitrile system are % nitrogen.

TABLE III
Copolymerization of *N*-*n*-Octadecylacrylamide (M_2) and
Various Monomers (M_1)

Monomer (M_1)	Con- version, %	Analysis			Rate of copoly- merization* R_p , mole/ kg-sec $\times 10^4$	
		M_2	C, %	m_2	Found	Calcd
Methyl methacrylate	6.25	0.0575	60.83	0.0151	0.21	0.28
	7.11	0.1085	61.46	0.0270	0.24	0.27
	6.23	0.1077	61.52	0.0282	0.21	0.27
	5.39	0.2089	63.42	0.0683	0.16	0.20
	4.82	0.2099	63.72	0.0752	0.15	0.20
	9.23	0.3078	65.27	0.1143	0.27	0.20
	7.08	0.3070	65.42	0.1184	0.21	0.20
	3.01	0.4069	66.45	0.1483	0.08	0.21
	7.57	0.4072	67.26	0.1740	0.21	0.21
	11.68	0.6059	70.84	0.3209	0.30	0.29
	11.46	0.6051	70.82	0.3199	0.29	0.29
	11.76	0.6890	72.74	0.4311	0.32	0.36
	15.67	0.6878	72.87	0.4398	—	—
	15.46	0.7020	73.10	0.4556	0.38	0.35
	12.45	0.7978	74.84	0.5965	—	—
Styrene	6.82	0.0513	90.85	0.0340	1.96	2.13
	7.38	0.0998	89.09	0.0839	2.03	1.95
	7.07	0.1611	89.16	0.0817	1.85	1.78
	7.30	0.3024	86.20	0.1912	1.63	1.54
	6.34	0.4018	84.69	0.2655	1.30	1.47
	6.91	0.5981	82.39	0.4171	1.36	1.47
	6.07	0.6979	80.99	0.5441	0.88	1.52
	8.72	0.7986	79.77	0.6884	1.63	1.59

* Calculated by using coefficients of Table IV for 60°C, except for styrene (80°C).

arise from perturbations in the Fineman and Ross variables caused by accumulated analytical errors. This effect was noticed before^{1,5} with long side-chain comonomers as $r_1 r_2$ approaches unity. Accordingly, plots of f_2 versus M_2 were fitted by an iterative method by setting $r_1 r_2 = 0.99$. Values of $r_1 = 3.00$ and $r_2 = 0.33$ were found to give the best fit. These were used to calculate Q_2 and e_2 in Table I, as well as to calculate a set of per cent carbon values for the various copolymers prepared. The calculated values were within experimental error of the per cent carbon values listed in Table III.

The reasons for the differences in e_2 between this work and that of Bork et al. are still not known. They may reside in small copolymer composition differences resulting from the analytical method employed (analysis for carbon used in this work; analysis for nitrogen used by Bork et al.). The data of Bork, where $r_1 r_2$ is 0.84 instead of unity as in this work, predicts greater alternation for amides with methyl methacrylate and less with styrene ($r_1 r_2$ is 0.54 instead of 0.28 in this work). The difference in the $r_1 r_2$ products between the two works is small however. The well known un-

certainties^{7b} in copolymer composition by the usual methods of analysis are probably responsible for the differences. It would seem that these sources of error can have an even greater effect on the isolation of penultimate group effects¹⁵ and consequently may result in their presence being masked in this work.

Rates of Copolymerization

Copolymerization rate data are presented in Tables II and III. Correlation of $R_p/[M][I]^{1/2}$ against composition enabled the drift in rate with composition to be ascertained under conditions simulating identical monomer and initiator concentrations. This correlation assumes the constancy of the quantity $R_p/[M][I]^{1/2}$ as the comonomer concentrations are changed at constant feed composition. The assumed constancy of this quantity is compatible with the effects of cross-termination,¹⁶ which affect rates as composition changes, because overall initiation equals overall termination under the steady-state conditions prevailing. Even if the ratio were not constant, the twofold change in concentration across the range of composition employed in this work would not introduce sufficient error to affect the desired correlation. However, the use of the rate data to estimate ϕ would be unwarranted in view of the uncertainties prevailing.¹⁶

Plots of $R_p/[M][I]^{1/2}$ against the mole fraction of long side-chain ester or amide (m_b) were curve-fitted by computer through a fifth-degree polynomial. A computed F test revealed that the second degree was the most significant. The coefficients and intercepts are given in Table IV. The

TABLE IV
Rate-Composition Coefficients for Selected Copolymers

M_1	M_2	$\frac{R_p/[M]}{[I]^{1/2}} \times 10^4$	$\alpha \times 10^4$	$\beta \times 10^4$
Methyl methacrylate	<i>n</i> -Octadecyl			
	acrylate	2.738	-2.928	7.609
"	Oleyl acrylate	2.051	-0.919	0.852
"	<i>N</i> - <i>n</i> -Octadecyl-			
	acrylamide	1.934	-4.409	9.192
Styrene	"	4.132	-1.891	7.781

magnitude and sign of these coefficients reveal that the rate data went through a minimum for all systems and that the extrapolated homopolymerization rate for the acrylamide and acrylate ester exceeded the rate for the other comonomers. An exception was oleyl acrylate, for which degradative allylic-type transfer presumably retarded rates at high fatty ester concentrations. The constants of Table IV were used to calculate the rates given in Tables II and III for the experimental concentrations. These may be considered smoothed data for the found values.

Experimental

All reagents, including the long-chain amine and alcohol and the commercial monomers, were 99% pure, usually as determined by gas-liquid chromatography.

The preparation and purification of *N*-*n*-octadecylacrylamide has been described.¹⁷ *n*-Octadecyl acrylate was prepared by the acylation of pure *n*-octadecanol by essentially the same procedure.¹⁷ The crude ester was treated with Skellysolve B (2 ml/g) to remove salt, washed with two 10% solutions of sodium carbonate (1 ml/ml), freed of alkali, and crystallized at -20°C . Recrystallization from acetone at 0°C (3 ml/g) gave the pure ester (98.5% pure by gas-liquid chromatography) mp $31.5\text{--}32.5^{\circ}\text{C}$, in 45.8% yields with the correct elementary analysis.

A similar procedure was followed for the oleyl acrylate, except that the Skellysolve B was removed after alkali washing and the crude product was crystallized once from acetone (3 ml/g) at -62°C . Purity was 94% by gas-liquid chromatography, the yield was 66%, and the correct elementary analysis was obtained. However, infrared analysis revealed that the ester was the equilibrium *cis-trans* mixture.

The purity of the starting oleyl alcohol was about 95% by gas-liquid chromatography; oleyl alcohol was predominantly in the *cis* form, indicating that the synthesis caused rearrangement.

The monomers were charged with analytic precision into suitably sized vessels under nitrogen and sealed. Where rates were determined, the initiator was added to the thermally equilibrated comonomers by a technique previously described.¹⁸ On an assumption of linearity of the conversion-time curve, the initial rate was estimated from the polymer weight. The monomer charge for the *n*-octadecyl acrylate copolymers with styrene and acrylonitrile was 30 g, the initiator was azobisisobutyronitrile (AIBN) (0.2 and 0.4 mole-%, respectively), and the solvent/monomer mole ratio was 4 except for the acrylonitrile, where the ratio was 3. *n*-Octadecyl acrylate was polymerized with methyl methacrylate, a charge of 15 g and a benzene/monomer mole ratio of one being used, while with oleyl acrylate, a 5-g charge was used at the same solvent/monomer ratio. A 5-g charge of long-chain amide and methyl methacrylate was utilized, and the benzene/monomer ratio was 3.91. In the amide-styrene system (15-g charge), benzene was used at a solvent/monomer ratio of 1. The initiator for these systems was AIBN (0.2%). Additional experimental data are given in Tables II and III. Analytical data were obtained at this laboratory and at a commercial laboratory and some samples were cross-checked.

The Fineman and Ross procedure¹⁹ was used, and r_1 was obtained as both slope and intercept. The values of r_1 and r_2 having the least error were reported. All calculations were written as programs for an IBM 1130 computer. Regression analysis was performed by program designation VGM58, usually carried through a fifth degree polynomial and programmed to yield an *F* test at each polynomial degree. Error was expressed as the

95% confidence limit. Other calculations were written for insertion into a general calculation subroutine designated QREAD.

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