EDMUND F. JORDAN, JR. and A. N. WRIGLEY, *Eastern Regional Research Laboratory, Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Philadelphia, Pennsylvania*

Synopsis

The monomer reactivity ratios and the corresponding copolymerization parameters for the copolymerization of *N*-octadecylacrylamide (M_1) and several monomers in *tert*-butyl alcohol at 60 ± 0.1°C. were determined and were: with acrylonitrile, $r_1 = 1.44 \pm 0.019$, $r_2 = 1.10 \pm 0.035$; $Q_1 = 0.60$, $e_1 = 1.20$; with vinylidene chloride, $r_1 = 1.37 \pm 0.008$, $r_2 = 0.438 \pm 0.008$; $Q_1 = 0.65$, $e_1 = 1.08$; with vinyl acetate, $r_1 = 6.11 \pm 0.045$, $r_2 = 0.027 \pm 0.009$; $Q_1 = 0.72$, $e_1 = 1.12$. The mean copolymerization parameters, therefore, were $Q_1 = 0.66$, $e_1 = 1.13$. The reactivity ratios and the corresponding copolymerization parameters for the copolymerization of *N*-allylstearamide (M_1) and several monomers, polymerized in *tert*-butyl alcohol at 80 ± 0.1°C. (except for vinyl acetate, polymerized in bulk at 70 ± 0.1°C.) were determined and were: with acrylonitrile, $r_1 = 0.118 \pm 0.084$, $r_2 = 3.61 \pm 0.087$; $Q_1 = 0.058$; $e_1 = 0.21$; with vinylidene chloride, $r_1 = 0 \pm 0.136$, $r_2 = 5.23 \pm 0.067$; $Q_1 = 0.028$, $e_1 = -0.80$; with vinyl acetate, $r_1 = 0.0532 \pm 0.012$, $r_2 = 0.740 \pm 0.087$; $Q_1 = 0.043$, $e_1 = -1.18$. The mean copolymerization parameters for *N*-allylstearamide were, therefore, $Q_1 = 0.043$, $e_1 = -0.59$.

INTRODUCTION

Few publications reporting the monomer reactivity ratios for either acrylic or allyl amides have appeared. In fact, a recent tabulation of about 900 reactivity ratios and Q and e parameters by Young[1a] failed to list a single example. Although copolymerization ratios for acrylamide and many comonomers have been determined in both aqueous and organic solvents,[1] similar data for *N*-substituted acrylamides have not been reported, and data for *N*,*N*-disubstituted acrylamides have been confined to a single copolymer system.[2] The results of that determination show that the substitution of two methyl groups for hydrogen appreciably affects the e parameter. Reactivity ratios for allylamides likewise are not in the literature in contrast with the situation for allyl esters, for which many published results are available.[1a]

As part of a systematic investigation of the polymerization properties of the higher *N*-substituted acrylamides and allylamides, the reactivity ratios of *N*-octadecylacrylamide and *N*-allylstearamide, each with three comonomers, were determined, and the corresponding Q and e parameters[3] were calculated. These are reported in Tables I and II, respectively.

Since the length of the alkyl chain has little effect on reactivity ratios,[4] the values listed in the tables may be considered to be representative of the respective homologous series.

TABLE I

Monomer Reactivity Ratios and Copolymerization Parameters for *N*-Octadecylacrylamide (M_1) and Various Monomers at 60°C.[a]

Monomer (M_2)	r_1	r_2	Q_1	e_1
Acrylonitrile	1.44 ± 0.019	1.10 ± 0.035	0.60[b]	1.20[b]
Vinylidene chloride	1.37 ± 0.008	0.438 ± 0.008	0.65	1.08
Vinyl acetate	6.11 ± 0.045	0.027 ± 0.009	0.72	1.12
		Mean value	0.66	1.13

[a] Q_2 and e_2 values taken from Young.[1a]
[b] A value of 1.00 assigned to r_1r_2.

TABLE II

Monomer Reactivity Ratios and Copolymerization Parameters for *N*-Allystearamide (M_1) and Various Monomers at 80°C.[a]

Monomer (M_2)	r_1	r_2	Q_1	e_1
Acrylonitrile	0.118 ± 0.084	3.61 ± 0.087	0.058	0.21
Vinylidene chloride	0 ± 0.136	5.23 ± 0.067	0.028[b]	−0.80[b]
Vinyl acetate[c]	0.532 ± 0.012	0.740 ± 0.087	0.043	−1.18
		Mean value	0.043	−0.59

[a] Q_2 and e_2 taken from Young.[1a]
[b] A small positive value of 0.05 was assigned to r_1.
[c] At 70°C.

DISCUSSION

N-Octadecylacrylamide Copolymerization

As can be seen in Table I, the Q and e parameters for *N*-octadecylacrylamide are in good internal agreement and thereby support the validity of the mean values listed. The average values, $e = 1.13$ and $Q = 0.66$ may be compared with those listed by Young[1a] for acrylamide ($e = 1.30$ and $Q = 1.18$). The vinyl group of *N*-octadecylacrylamide thus appears to have similar or slightly greater electron density (slightly less positive value of e) and to be somewhat less reactive toward attacking radicals (smaller value of Q). It is still much more electron-poor than that of *N*,*N*-dimethylacrylamide ($e = -0.26$), copolymerized by Saini[2] with acrylic acid, and the reason for the large effect of the second *N* alkyl group is not known. It is of additional interest that acrylic acid bears the same relationship to its esters (higher value of Q in the former; similar value in both for e) as does acrylamide to the *N*-substituted acrylamide reported here.

The unlikely value of $r_1r_2 = 1.6$, found for the acrylonitrile system in Table I is probably the result of small analytical errors. Although 12 experimental points were determined, slightly low values for nitrogen content, found for all six experiments at high amide concentrations, resulted

in higher than expected values of f for these particular experiments. This caused a slight upward shift in the slope (r_1) of the Fineman-Ross plot as well as a corresponding drop in the value of the intercept (r_2). In addition, deviations in individual experimental points were greater for this system than for the other two copolymerizations listed in the table. The more probable product value 1.00 was used to compute the corresponding Q and e parameters.

N-Allylstearamide Copolymerization

Copolymers of allylstearamide and vinyl acetate were in general too soluble to isolate by precipitation with a nonsolvent. Consequently a method of determining the values of m_1 and m_2 indirectly by chemical analysis of the reaction product was worked out and is detailed in the experimental section.

The overall results show that *N*-allylstearamide behaves similarly to allyl esters in copolymerization.

EXPERIMENTAL

Reagents

N-Octadecylacrylamide was prepared by the acylation of octadecylamine of 90% purity by a slight excess of acrylyl chloride in benzene (18.5 ml./g. amine) at 37°C., triethylamine being used as the acid scavenger. After filtration and removal of solvent, the crude product was crystallized once from Skellylsolve B and four times from acetone (10 ml./g.) at room temperature to give the amide, 98.5% pure by gas liquid chromatography, in 38% yield; carbon, calcd. 77.93%, found 77.98%; hydrogen, calcd. 12.80%, found 12.84%; nitrogen calcd. 4.33%, found 4.33%. Reproducible melting points were obtained only by determination from melted samples because of marked polymorphism exhibited by this amide. The capillary melting point was 73.5–74.0°C.

The isomer, *N*-allylstearamide, was made by the method of Jordan and Port;[5] capillary melting point 83.8–84.3°C., found values: carbon, 77.98%; hydrogen 12.94%; nitrogen, 4.33%. Purity by gas liquid chromatography was greater than 99%.

The other monomers and solvents were from commercial sources and were distilled through a Widmer Column before use. Refractive index and boiling point were taken as the criteria of purity.

Copolymerization of *N*-Octadecylacrylamide

All copolymerizations were conducted at 60 ± 0.1°C. in *tert*-butyl alcohol (4 moles/mole of total monomer) in sealed 7-oz. bottles, with 15 g. total monomer and 0.2–0.4 mole-% benzoyl peroxide as the initiator. The copolymers were isolated and extracted free of monomer with excess hot methanol. Table III summarizes the experimental data.

The Fineman and Ross equation[7] was used to calculate the reactivity ratios reported in Table I.

TABLE III
Copolymerization of N-Octadecylacrylamide $(M)_1$ and Various Monomers (M_2)

Monomer (M_2)	Sample no.	Conversion, %	Analysis[a] M_1	%	m_1
Acrylonitrile	1	4.2	0.0701	19.44	0.0687
	2	3.7	0.0701	19.28	0.0724
	3	3.7	0.1412	15.93	0.1375
	4	7.3	0.1381	15.77	0.1323
	5	3.9	0.2123	13.29	0.2019
	6	8.3	0.2077	13.36	0.1915
	7	2.1	0.2804	10.99	0.3076
	8	10.0	0.2766	10.66	0.2896
	9	2.5	0.4198	8.16	0.4385
	10	4.4	0.4125	7.87	0.4611
	11	5.7	0.5608	6.40	0.6130
	12	5.5	0.5503	6.63	0.5850
Vinylidene chloride	1	0.31	0.0717	47.40	0.1399
	2	1.6	0.1432	33.59	0.2608
	3	3.5	0.2121	26.49	0.3454
	4	10.0	0.2865	21.28	0.4222
	5	10.9	0.2860	21.08	0.4253
	6	3.9	0.4326	14.01	0.5584
	7	9.7	0.5694	9.04	0.6800
Vinyl acetate	1	9.4	0.0699	74.07	0.5482
	2	10.5	0.0689	74.35	0.5780
	3	1.1	0.1405	75.89	0.7217
	4	5.7	0.2108	76.59	0.8025
	5	1.2	0.2745	76.59	0.8025
	6	1.1	0.4201	76.59	0.8025
	7	3.0	0.5560	77.42	0.9154

[a] For the acrylonitrile system the Kjeldahl nitrogen method was used; for the vinylidene chloride system, Carius chloride determination; for the vinyl acetate system, carbon was determined by microcombustion.

Copolymerization of N-Allylstearamide with Acrylonitrile and with Vinylidene Chloride

Copolymerizations were conducted at 80 ± 0.1°C. in *tert*-butyl alcohol, (4 moles/mole total monomer), 15 g. of total monomer and 0.25–1.0 mole-% benzoyl peroxide as the initiator being used. Increased amounts of initiator were used with increased amide content of the monomer feed. Monomers were charged with analytical precision into 7-oz. bottles in a nitrogen atmosphere and capped. The copolymers were isolated by precipitation with a large excess of methanol (60 ml./g.) at 30°C. and extracted several times with hot methanol (10 ml./g.) until free of monomer.

Copolymerization of N-Allylstearamide with Vinyl Acetate

Monomers (15 g. total weight) were charged with analytical precision into heavy-walled tubes which were closed and heated at 70°C. until the amide dissolved. Above 40 mole-% of amide, small portions (2–8 ml.) of benzene had to be added to maintain solution at 70°C. An amount of benzoyl peroxide, calculated from dM/dP data on a similar system to yield a

5% conversion to polymer, was added to the homogeneous mixture at 70°C., the tubes closed immediately, and the polymerization conducted at 70 ± 0.1°C. (It was found experimentally that no loss of vinyl acetate occurred by volatilization with this technique.)

The volatile monomer (and benzene, if present) was removed by evaporation at room temperature to yield a crude reaction mixture. The moles of amide and ester in the copolymer (m_1 and m_2), present in this mixture, were calculated from determinations of iodine number and ester number. The iodine number determined unreacted amide, and this, on subtraction

TABLE IV
Copolymerization of *N*-Allylstearamide (M_1) and Various Monomers (M_2)

Monomer (M_2)	Sample no.	Conversion, %	Analysis[a] M_1	%	m_1
Acrylonitrile	1	6.8	0.1401	21.48	0.0449
	2	3.0	0.1423	21.77	0.0417
	3	10.0	0.2812	18.23	0.0879
	4	10.5	0.4111	14.81	0.1535
	5	8.7	0.4204	14.85	0.1526
Vinylidene chloride	1	4.8	0.1049	68.36	0.0205
	2	8.1	0.1792	64.02	0.0410
	3	2.3	0.2138	62.78	0.0471
	4	3.5	0.2429	62.51	0.0485
	5	2.0	0.2875	59.68	0.0633
	6	3.6	0.3543	58.02	0.0724
	7	1.5	0.4266	53.54	0.0989
Vinyl acetate	1	10.2	0.1006	Titrimetric	0.0897
	2	10.9	0.2063	"	0.1886
	3	8.9	0.2996	"	0.3157
	4	6.5	0.4028	"	0.4108
	5	7.9	0.4967	"	0.5163
	6	7.2	0.6047	"	0.5906
	7	6.7	0.7061	"	0.6288
	8	7.9	0.8056	"	0.7281

[a] Methods of analysis as in Table III except for the vinyl acetate system. For vinyl acetate, titrametric data were obtained as follows. Initial moles amide, weight residue, iodine Number of residue, saponification number of residue, acid number of residue, respectively; sample 1: 0.013617, 5.5456, 56.4309, 130.9777, 0.8472; sample 2: 0.02244, 8.1854, 62.7233, 70.3282, 2.1599; sample 3: 0.02843, 9.7430, 67.6190, 35.0674, 2.5080; sample 4: 0.03313, 10.9984, 71.5032, 17.7628, 1.9629; sample 5: 0.03656, 12.1566, 70.6615; 15.6759, 2.9736; sample 6: 0.03934, 12.9913, 71.4549, 11.5595, 3.1165; sample 7: 0.04154, 13.6823, 72.7284, 9.7462, 3.3244; sample 8: 0.04334, 14.3214, 71.7173, 9.5992, 4.4722.

from the initial amide, indicated the octadecylacrylamide present in the copolymer. The ester number determined the ester content of the copolymer. An acid number corrected the saponification number for benzoic acid resulting from degradative chain transfer,[6] a reaction which accounted for 40–50 mole-% of the initiator decomposition. A small error, introduced by the uncertain fate of the remaining initiator, was neglected. *N*-Allylstearamide was unaffected by the conditions of ester saponification used.

The essential data are summarized in Table IV for all *N*-allylstearamide copolymerizations studied. The Fineman and Ross equation[7] was used to calculate the reactivity ratios reported in Table II.

The authors thank Mr. James Harrison and Mr. Theodore Defosse for assistance in the preparation of copolymers and Mrs. Ruth B. Kelly for the analytical determinations.

References

1. (a) Young L. J., *J. Polymer Sci.*, **54**, 411 (1961); (b) M. Matsuda, T. Otsu, and M. Imoto, *Kobunshi Kagaku* **16**, 437 (1959); (c) M. Imoto, T. Otsu, and T. Highuchi, *ibid.*, **16**, 324 (1959); (d) H. Kamogawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **61**, 1024 (1958).
2. Saini, G., G. Polla-Mattiot, and M. Meirone, *J. Polymer Sci.*, **50**, S12 (1961).
3. Alfrey, T., Jr., and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).
4. Jordan, E. F., Jr., K. M. Doughty, and W. S. Port, *J. Appl. Polymer Sci.*, **4**, 203 (1960).
5. Jordan, E. F., Jr., and W. S. Port, *J. Am. Oil Chemists' Soc.*, **38**, 600 (1961).
6. Bartlett, P. D., and R. Altschul, *J. Am. Chem. Soc.*, **67**, 812 (1945); *ibid.*, **67**, 816 (1945).
7. Fineman, M., and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).

Résumé

Les réactivités des monomères et les paramètres de copolymérisation correspondants pour la copolymérisation du *N*-octadécylacrylamide (M_1) et de différents monomères dans l'alcool *t*-butylique à 60 ± 0.10°C, ont été déterminés et sont les suivants: avec l'acrylonitrile, $r_1 = 1.44 \pm 0.19$; $r_2 = 1.10 \pm 0.0335$; $Q_1 = 0.60$, $e_1 = 1.20$; avec le chlorure de vinylidène, $r_1 = 1.37 \pm 0.008$; $r_2 = 0.438 \pm 0.008$; $Q_1 = 0.65$, $e_1 = 1.08$; avec l'acétate de vinyle, $r_1 = 6.11 \pm 0.045$; $r_2 = 0.027 \pm 0.009$; $Q_1 = 0.72$, $e_1 = 1.12$. Les paramètres de copolymérisation étaient donc $Q_1 = 0.66$, $e_1 = 1.13$. Les rapports de réactivité et les paramètres correspondants de la copolymérisation pour la copolymerisation de *N*-allylstéaramide (M_1) et différents monomères polymérisés dans l'alcool *t*-butylique à 80° ± 0.1°C (excepté pour l'acétate de vinyle, polymérisé en bloc à 70 ± 0.1°C) ont été déterminés et étaient: pour l'acrylonitrile, $r_1 = 0.118 \pm 0.084$, $r_2 = 3.61 \pm 0.087$; $Q_1 = 0.058$, $e_1 = 0.21$; pour le chlorure de vinylidène $r_1 = 0.-0.136$, $r_2 = 5.23 \pm 0.067$, $Q_1 = 0.028$, $e_1 = -0.80$; pour l'acétate de vinyle, $r_1 = 0.532 \pm 0.012$, $r_2 = 0.740 \pm 0.087$, $Q_1 = 0.043$, $e_1 = -1.18$. Les paramètres de la copolymérisation pour la *N*-allylstéaramide furent donc: $Q_1 = 0.043$, $e_1 = -0.59$.

Zusammenfassung

Die Monomer-Reaktivitätsverhältnisse und die entsprechenden Copolymerisationsparameter wurden für die Copolymerisation von *N*-Octadecylacrylamid (M_1) mit mehreren Monomeren in *t*-Butylalkohol bei 60 ± 0,1°C bestimmt. Folgende Werte wurden gefunden: mit Acrylnitril, $r_1 = 1{,}44 \pm 0{,}019$, $r_2 = 1.10 \pm 0{,}035$; $Q_1 = 0{,}60$, $e_1 = 1{,}20$; mit Vinylidenchlorid, $r_1 = 1{,}37 \pm 0{,}008$, $r_2 = 0{,}438 \pm 0{,}008$; $Q_1 = 0{,}65$, $e_1 = 1{,}08$; mit Vinylacetat, $r_1 = 6{,}11 \pm 0{,}045$, $r_2 = 0{,}027 \pm 0{,}009$; $Q_1 = 0{,}72$, $e_1 = 1{,}12$. Der Mittelwert für die Copolymerisationsparameter ist daher: $Q_1 = 0{,}66$, $e_1 = 1{,}13$. Die Reaktivitätsverhältnisse und die entsprechenden Copolymerisationsparameter für die Copolymerisation von *N*-Allylstearamid (M_1) mit mehreren Monomeren in *t*-Butylalkohol bei 80 ± 0 1°C (mit Ausnahme von Vinylacetat das in Substanz bei 70 ± 0,1°C polymerisiert wurde) bestimmt. Es ergaben sich folgende Werte: mit Acrylnitril, $r_1 = 0{,}118 \pm 0{,}084$, $r_2 = 3{,}61 \pm 0{,}087$; $Q_1 = 0{,}058$, $e_1 = 0{,}21$; mit Vinylidenchlorid, $r_1 = 0{,}60 \pm 0{,}136$, $r_2 = 5{,}23 \pm 0{,}067$; $Q_1 = 0{,}028$; $e_1 = -0{,}80$; mit Vinylacetat, $r_1 = 0{,}532 \pm 0{,}012$, $r_2 = 0{,}740 \pm 0{,}087$; $Q_1 = 0{,}043$, $e_1 = -1{,}18$. Der Mittelwert für die Copolymerisationsparameter ist daher für *N*-allylstearamid: $Q_1 = 0{,}043$, $e_1 = -0{,}59$.

Received November 19, 1962