

Nitrogen-Containing Monomers. III. Reactivity Ratios of *N*-Alkyl Acrylamides with Vinyl Monomers

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INTRODUCTION

Many reports concerning *N*-alkyl acrylamides have appeared in the literature^{1a-d} but no studies of their reactivities in copolymerization reactions have been disclosed. We have examined *N*-*tert*-octyl acrylamide, *N*-*n*-octyl acrylamide, and *N,N*-di-*n*-butyl acrylamide in order to study the effects of substitution and branching on the copolymerization reactivity. This paper describes the reactivity ratio determinations obtained from these acrylamides with styrene and methyl methacrylate. The Aifrey-Price *Q* and *e* values were calculated for the three monomers, to complete the comparison.

EXPERIMENTAL

Monomers

The *N*-*tert*-octyl acrylamide [actually *N*-(1,1,3,3-tetramethylbutyl) acrylamide] was prepared from diisobutylene and acrylonitrile according to the general procedure used by Ritter and Minieri.^{1a} The crude monomer was distilled at 80°C. (0.3 mm.) and gave pure product in 40% yield (calcd. for C₁₁H₂₁ON, N 7.65%; found, N 7.52%).

The *N*-*n*-octyl acrylamide was prepared by the reaction of *n*-octylamine with acrylyl chloride in the presence of a 10% solution of NaOH in water. The crude monomer was extracted with benzene and distilled at 102°C. (0.05 mm.); this gave pure monomer in 67% yield (calcd. for C₁₁H₂₁ON, N 7.65%; found, N 7.61%).

The *N,N*-di-*n*-butyl acrylamide was prepared by the reaction of di-*n*-butylamine with acrylyl chloride in the presence of triethylamine. The crude material distilled at 60°C. (0.06 mm.) gave pure monomer in 64% yield (calcd. for C₁₁H₂₁ON, N 7.65%; found, N 7.61%).

The styrene and methyl methacrylate were commercial-grade materials which were carefully distilled before use.

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TABLE I. Reactivity Ratio Data for Styrene (M_1) and Acrylamides (M_2): Solution Polymerization in Benzene at 50°C.

$\begin{array}{c} R_1 \\ \diagdown \\ N-N-C(O)-CH=CH_2 \\ \diagup \\ R_2 \end{array}$		Charge			Product		
		M_1 , g.	M_2 , g.	M_2 fraction, mole	Convsn., %	N, %	M_2 fraction, mole
<i>tert</i> -Oct	H	15.77	9.23	0.25	6.3	1.26	0.101
<i>tert</i> -Oct	H	11.51	13.49	0.49	5.8	2.21	0.187
<i>tert</i> -Oct	H	9.06	15.94	0.50	9.8	2.91	0.259
<i>tert</i> -Oct	H	6.87	18.13	0.60	6.5	3.49	0.323
<i>tert</i> -Oct	H	4.90	20.10	0.70	3.2	4.42	0.437
<i>n</i> -Oct	H	19.07	5.93	0.150	4.4	0.77	0.060
<i>n</i> -Oct	H	15.74	9.26	0.250	3.8	1.33	0.107
<i>n</i> -Oct	H	12.88	12.17	0.349	3.6	1.98	0.166
<i>n</i> -Oct	H	11.50	13.50	0.400	2.3	2.14	0.181
<i>n</i> -Oct	H	9.09	15.97	0.502	6.5	3.09	0.278
<i>n</i> -Oct	H	5.97	19.30	0.648	6.3	4.05	0.390
<i>n</i> -Oct	H	4.90	20.10	0.700	0.7	4.18	0.407
<i>n</i> -But	<i>n</i> -But	20.91	4.09	0.100	15.7	0.84	0.066
<i>n</i> -But	<i>n</i> -But	17.35	7.65	0.200	10.7	1.57	0.128
<i>n</i> -But	<i>n</i> -But	14.25	10.75	0.300	9.5	2.28	0.194
<i>n</i> -But	<i>n</i> -But	11.60	13.60	0.400	11.2	3.00	0.268
<i>n</i> -But	<i>n</i> -But	7.95	17.05	0.550	10.7	3.95	0.378
<i>n</i> -But	<i>n</i> -But	4.90	20.10	0.700	13.1	4.99	0.525

TABLE II. Reactivity Ratio Data for Methyl Methacrylate (M_1) and Acrylamides (M_2) Solution Polymerization in Benzene at 50°C.

$\begin{array}{c} R_1 \\ \diagdown \\ N-N-C(O)-CH=CH_2 \\ \diagup \\ R_4 \end{array}$		$\begin{array}{c} R_2 \\ \diagdown \\ CH \\ \diagup \\ \end{array}$		Charge		Product	
R_1	R_2	M_1 , g.	M_2 , g.	M_2 fraction, mole	Convsn., %	N, %	M_2 fraction, mole
<i>tert</i> -Oct	H	22.68	7.32	0.150	10.6	0.65	0.048
<i>tert</i> -Oct	H	20.19	9.81	0.210	7.5	0.93	0.070
<i>tert</i> -Oct	H	17.52	12.54	0.281	6.0	1.24	0.096
<i>tert</i> -Oct	H	15.11	15.04	0.352	4.6	1.76	0.140
<i>tert</i> -Oct	H	12.02	17.99	0.450	7.0	2.25	0.185
<i>tert</i> -Oct	H	9.29	20.75	0.550	5.3	2.94	0.255
<i>tert</i> -Oct	H	6.83	23.16	0.650	1.5	3.55	0.521
<i>tert</i> -Oct	H	4.69	25.59	0.749	2.8	4.65	0.459
<i>n</i> -Oct	H	17.18	7.93	0.202	14.0	0.95	0.071
<i>n</i> -Oct	H	15.52	9.48	0.250	12.4	1.21	0.093
<i>n</i> -Oct	H	12.80	12.40	0.350	9.4	1.71	0.136
<i>n</i> -Oct	H	8.88	16.18	0.498	4.2	2.55	0.215
<i>n</i> -Oct	H	5.72	19.44	0.651	14.0	4.07	0.383
<i>n</i> -But	<i>n</i> -But	20.78	4.22	0.100	9.1	0.82	0.062
<i>n</i> -But	<i>n</i> -But	17.15	7.85	0.200	14.9	1.56	0.123
<i>n</i> -But	<i>n</i> -But	14.00	11.00	0.300	18.9	2.31	0.191
<i>n</i> -But	<i>n</i> -But	11.27	13.73	0.400	14.7	2.97	0.258
<i>n</i> -But	<i>n</i> -But	7.74	17.26	0.550	3.6	4.08	0.385
<i>n</i> -But	<i>n</i> -But	4.75	20.25	0.700	5.4	5.18	0.536

Polymerizations

The experiments were run essentially by the methods of Mayo and Lewis.² Polymerizations were carried out in 4-oz. screw-cap bottles fitted with polyethylene gaskets, under a nitrogen atmosphere, and with 0.50 wt.-% azobisisobutyronitrile as initiator. The polymers were made to precipitate by pouring the solutions into a nonsolvent, and were purified by repeated reprecipitations from a solvent system to a nonsolvent system. The purified polymers were dried to constant weight under high vacuum, and the compositions were determined by elemental analysis. The per cent nitrogen was determined by a micro-Dumas procedure.

The reactivity ratios were determined from the differential form of the general copolymerization equation both by the method of intercepts³ and the Fineman-Ross plots.⁴

Reactivity Ratio Determinations

N-tert-Octyl Acrylamide

With Styrene. Copolymers of *N-tert-octyl acrylamide* (M_2) and styrene (M_1) were prepared in benzene solution and precipitated with methanol. The copolymers were purified from benzene-methanol. Table I gives the results. The r_1 and r_2 values obtained were $r_1 = 2.8$ and $r_2 = 0.25$.

With Methyl Methacrylate. The copolymerizations of *N-tert-octyl acrylamide* (M_2) with methyl methacrylate (M_1) were run in benzene solution and precipitated with naphtha. Purification was by reprecipitation from benzene-naphtha. Results are shown in Table II. Reactivity ratio values of $r_1 = 3.60$ and $r_2 = 0.24$ were obtained.

N-n-Octyl Acrylamide

With Styrene. The benzene solution copolymerizations of *N-n-octyl acrylamide* (M_2) with styrene (M_1) are described in Table I. The copolymers were precipitated with methanol and purified by reprecipitation from benzene-methanol. From the data, values of $r_1 = 2.70$ and $r_2 = 0.20$ were calculated.

With Methyl Methacrylate. The copolymerization data of *N-n-octyl acrylamide* (M_2) with methyl methacrylate (M_1) in benzene solution are given in Table II. Naphtha was used to precipitate the polymers, and they were purified from benzene-naphtha. Values of $r_1 = 3.50$ and $r_2 = 0.24$ were calculated for the pair.

N,N-di-n-Butyl Acrylamide

With Styrene. The copolymers of *N,N-di-n-butyl acrylamide* (M_2) and styrene (M_1) (see Table I) were prepared by solution polymerization in benzene and precipitated in methanol. Reprecipitation was from benzene-methanol. Reactivity ratios determined from the data were $r_1 = 1.65$ and $r_2 = 0.32$.

TABLE III. Reactivity Ratios and Q and e Values of *N-tert-Octyl Acrylamide*, *N-n-Octyl Acrylamide*, and *N,N-di-n-Butyl Acrylamide*

M_1	M_2	r_1	r_2	Q_1	e_1	Q_2	e_2
Styrene	<i>N-tert-Octyl acrylamide</i>	2.8 ± 0.10	0.25 ± 0.06	1.0	-0.8	0.22	-0.21
Methyl methacrylate	<i>N-tert-Octyl acrylamide</i>	3.6 ± 0.04	0.24 ± 0.04	0.74	+0.4	0.19	+0.02
Styrene	<i>N-n-Octyl acrylamide</i>	2.70 ± 0.10	0.20 ± 0.05	1.0	-0.8	0.19	-0.02
Methyl methacrylate	<i>N-n-Octyl acrylamide</i>	3.50 ± 0.06	0.24 ± 0.06	0.74	+0.4	0.17	-0.17
Styrene	<i>N,N-di-n-Butyl acrylamide</i>	1.65 ± 0.03	0.32 ± 0.02	1.0	-0.8	0.32	0.0
Methyl methacrylate	<i>N,N-di-n-Butyl acrylamide</i>	1.85 ± 0.05	0.42 ± 0.04	0.74	+0.4	0.33	+0.14
Acrylic acid	Acrylamide	1.43 ± 0.03	0.60 ± 0.02	0.75	1.0	0.61	+0.75
Acrylic acid	Acrylamide	0.36	1.38	—	—	0.92	+0.48
Acrolein	Acrylamide	2.0 ± 0.05	0.76 ± 0.02	0.55	0.88	0.6	1.0

With Methyl Methacrylate. Table II describes the copolymerization of *N,N*-di-*n*-butyl acrylamide (M_2) with methyl methacrylate (M_1). Polymerizations were carried out in benzene, and polymers were precipitated in naphtha and purified by reprecipitation from benzene-naphtha. Calculation of reactivity ratios from the data gave $r_1 = 1.85$ and $r_2 = 0.42$.

DISCUSSION

The results of the reactivity ratio determinations are summarized in Table III. The copolymers of all three substituted acrylamides with styrene and methyl methacrylate contain smaller amounts of substituted acrylamide than the charge. This can be seen from the relatively higher r_1 and lower r_2 values. The particular compounds used in this study were purposely chosen to eliminate any effects which might arise from changes in size, volume, or mass of substituents.

Comparison of the reactivity ratios of *N-tert*-octyl acrylamide and of *N-n*-octyl acrylamide shows no significant difference. This indicates that branching on the alkyl substituent has little influence on the polymerization characteristics of these monomers. Although the *tert*-octyl derivative greatly hinders the amide function, as demonstrated by the resistance of the amide to acid- or base-catalyzed hydrolysis,¹⁶ an inspection of the Fisher-

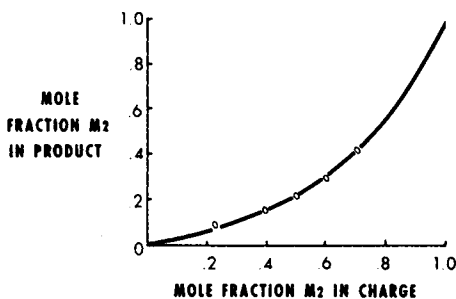


Fig. 1. Composition curve for copolymers of styrene (M_1) and *N-tert*-octyl acrylamide (M_2).

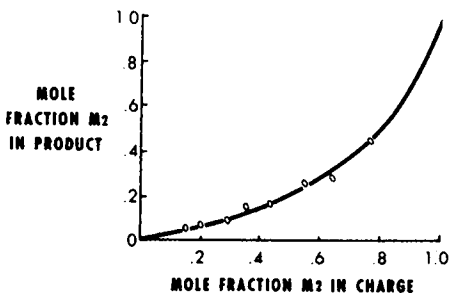


Fig. 2. Composition curve for copolymers of methyl methacrylate (M_1) and *N-tert*-octyl acrylamide (M_2).

Taylor-Hirschfelder model shows the vinyl group to be pendant and free from hindrance.

When *N-tert*-octyl acrylamide and *N-n*-octyl acrylamide are compared with *N,N*-di-*n*-butyl acrylamide, an appreciable difference in reactivity is noted. The disubstituted monomer shows a considerably increased reactivity over the monosubstituted monomers, the r_1 values being lower and the r_2 and Q_2 values being higher. This can be seen graphically in the composition curves of the various copolymers, shown in Figures 1-6.

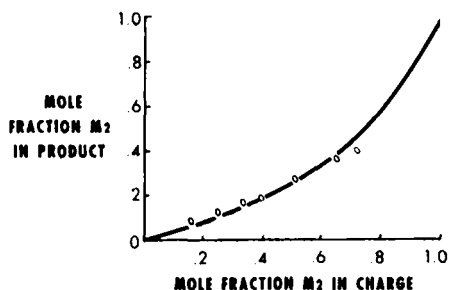


Fig. 3. Composition curve for copolymers of styrene (M_1) and *N-n*-octyl acrylamide (M_2).

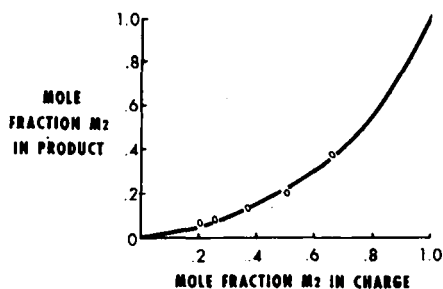


Fig. 4. Composition curve for copolymers of methyl methacrylate (M_1) and *N-n*-octyl acrylamide (M_2).

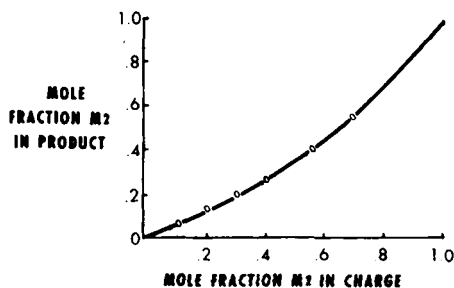


Fig. 5. Composition curve for copolymers of styrene (M_1) and *N,N*-di-*n*-butyl acrylamide (M_2).

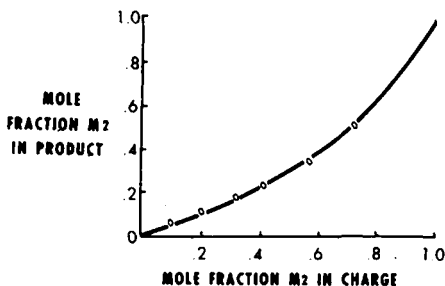


Fig. 6. Composition curve for copolymers of methyl methacrylate (M_1) and N,N -di- n -butyl acrylamide (M_2).

The Alfrey-Price equations were used to calculate the Q and e values listed in Table III. For N -*tert*-octyl acrylamide, average values of $Q = 0.20$ and $e = -0.10$ were found, while those for N - n -octyl acrylamide were $Q = 0.18$ and $e = -0.07$. The average values for N,N -di- n -butyl acrylamide were $Q = 0.32$ and $e = 0.07$. Thus it appears that the disubstituted monomer is more reactive than either the branched or straight-chain monosubstituted derivatives, the latter two being essentially of equal reactivity. Qualitatively, this may be because the donation of electronic charge to a resonance-stabilized intermediate radical is greater by a disubstituted nitrogen than by a monosubstituted nitrogen.

While there is some disagreement in the literature concerning the reactivity of acrylamide itself ($Q = 0.61$, $e = 0.75$; $Q = 0.92$, $e = 0.48$; $Q = 0.60$, $e = 1.0$),^{5,6,7} the values indicate that it is considerably more reactive than the substituted acrylamides reported here. The greater reactivity of the unsubstituted derivative may be, at least in part, a consequence of the greater crowding of atoms in a resonance-stabilized intermediate which has the double bond adjacent to substituted nitrogen. Approximate models of such structures show this to be the case when alkyl groups replace the hydrogens bonded to nitrogen. This trend appears also in methyl and ethyl methacrylamide ($Q = 0.32$, $e = -0.60$; $Q = 0.25$, $e = -0.88$, respectively).⁸

From the work reported here it may be concluded that the reactivities of the highly branched N -*tert*-octyl acrylamide and linear N - n -octyl acrylamide are essentially the same, while both are less reactive than N,N -di- n -butyl acrylamide.

We are indebted to Mr. Harry Ferber and Mr. Zenowie Holubec of our Analytical Department for the polymer analysis. We also wish to thank Mr. David Vincent for many helpful discussions concerning this work.

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Synopsis

The reactivity ratios in the copolymerizations of *N-tert*-octyl acrylamide, *N-n*-octyl acrylamide, and *N,N*-di-*n*-butyl acrylamide with styrene and methyl methacrylate have been determined, and the Alfrey-Price Q and e values calculated. The distributed monomer *N,N*-di-*n*-butyl acrylamide was found to be more reactive than either *N-n*-octyl or *N-tert*-octyl acrylamide, which were of about the same reactivity.

Résumé

On a déterminé les rapports de réactivité dans les copolymérisations de *N-tert*-octylacrylamide, de *N-n*-octylacrylamide et de *N,N*-di-*n*-butylacrylamide avec le styrène et le méthacrylate de méthyle et on a calculé les valeurs Q et e de l'équation de Alfrey-Price. On a trouvé que le monomère disubstitué *N,N*-di-*n*-butylacrylamide était plus réactionnel que le *N-n*-octylacrylamide ou le *N-tert*-octylacrylamide qui présentaient à peu près la même réactivité.

Zusammenfassung

Die Reaktivitätsverhältnisse bei der Copolymerisation von *N-tert*-Octylacrylamid, *N-n*-Octylacrylamid und *N,N*-Di-*n*-butylacrylamid mit Styrol und Methylmethacrylat wurden bestimmt und die Q - und e -Werte nach Alfrey und Price berechnet. Das disubstituierte Monomere, *N,N*-Di-*n*-butylacrylamid zeigt eine höhere Reaktivität als *N-n*-Octyl- und *N-tert*-Octylacrylamid, die etwa die gleiche Reaktivität besaßen.

Received September 25, 1961