

COMPOSITIONAL HETEROGENEITY OF BUTADIENE-ACRYLONITRILE COPOLYMERS PREPARED IN EMULSION AT 5°C.¹

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Abstract

The copolymerization of butadiene and acrylonitrile is very similar to the copolymerization of butadiene and styrene. Polymers predominantly butadiene may be studied by conventional solution techniques but the study of polymers rich in acrylonitrile requires improved solvents for these materials. Polymerization rates are greatest for monomer ratios approximating equal proportions. The mercaptan modifier disappears much more slowly than in the butadiene-styrene system, the regulating index approximating unity. The number average molecular weights calculated from the mercaptan disappearance curves indicate uniform polymer molecular weights to relatively high conversions after which there is a decrease. The viscosity data indicate a rise in viscosity with conversion, which effect is overcome for charges rich in acrylonitrile by the lessening of branching, the more rapid disappearance of mercaptan at high conversion, and the tendency of polymers containing over 50% acrylonitrile to show very low dilute solution viscosities in the solvents tested. Viscosity molecular weights have been calculated and estimates of the molecular weight distribution made. These distributions appear to be quite narrow and the usual broadening at higher conversions is prevented by the increased modifier consumption and increased vinyl content of the polymer prepared with 50 parts acrylonitrile in the charge. The bound acrylonitrile has been determined at various conversions and the reactivity ratios have been found to be $r_1 = 0.28$ and $r_2 = 0.02$ for emulsions and $r_1 = 0.18$ and $r_2 = 0.03$ for oil phase portion only. Q is 0.74 and e is 1.47 as calculated by the Alfrey-Price equations.

Introduction

Many acrylonitrile polymers and copolymers have been studied but the data published on the emulsion copolymerization of butadiene and acrylonitrile are scarce. The most directly useful results are those of Wall (23, 24) and of Semon (19, 20). Some data obtained during the copolymerization of other monomers with acrylonitrile (4, 5, 6, 9, 15) may be used to calculate the approximate behavior of the butadiene-acrylonitrile system. The purpose of this work is to co-ordinate the data and to fill in the gaps in the published information.

The butadiene-acrylonitrile system is complicated by two factors. The polymer is insoluble in butadiene which may make the oil phase portion of the system heterogeneous. Acrylonitrile is appreciably soluble in water and is extremely reactive towards many common materials such as mercaptan, peroxides, amines, etc. Thus the distribution of acrylonitrile between the oil and water phases and its interaction with polymerization recipe ingredients must be considered.

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Two series of experiments were conducted some years apart. In the first a recipe similar to one used for butadiene-styrene studies was used (see (13)). When interest became centered around low temperature polymerizations to yield better and more uniform butadiene-styrene copolymers, the activated recipes (see (12, 22)) were applied successfully to the butadiene-acrylonitrile system.

Techniques

The polymerization technique was that generally used in the rubber industry (3, 12, 13, 16, 22). Modifier disappearance curves and intrinsic viscosities were determined conventionally (16). Bound acrylonitrile was estimated by Kjeldahl nitrogen determinations. The fractionation curves were prepared from the usual solvent-nonsolvent precipitation procedure (see (14)). Gel (3, 13) was considered as all insoluble material in the particular solvent, and the swelling index (3, 13) as the ratio of the weight of swollen gel to weight of polymer in the gel. The dilute solution viscosity (3, 13) was measured on the soluble portion of the dry polymer. Monomer charge ratios are weight to weight, which with butadiene and acrylonitrile are very nearly mole to mole.

Experimental

Dilute Solution Viscosity and Gel of Polymers Prepared at 30°C.

The effect of degree of conversion on the solution properties of polymers is shown in Table I. The gel and swelling index remain relatively constant but

TABLE I
EFFECT OF CONVERSION ON THE GEL, SWELLING INDEX, AND DILUTE SOLUTION VISCOSITY

Time (hr.)	% Conversion	% Gel	Swelling index	Dilute solution viscosity
			in chlorobenzene solution	
71.5/28.5 charge ratio butadiene to acrylonitrile				
4	37.1	49	65	2.88
6	46.2	46	50	2.74
8	57.3	44	82	2.64
11	68.2	70	67	3.49
15	80.1	46	53	1.92
20	86.7	41	52	0.84
60/40 charge ratio butadiene to acrylonitrile				
3	22	12	19	1.95
5	56.6	25	41	2.84
7	77.7	49	49	1.73
10	93.7	72	38	0.91
14	96.2	94	31	0.86
19	96.8	94	26	0.82

the dilute solution viscosity of the soluble portion rises to a maximum and then decreases. Somewhat similar results are obtained for the dilute solution viscosity of a 60-40 butadiene-acrylonitrile charge. There tends to be an increase in the amount of gel with conversion more in keeping with the lower dilute solution viscosity. The latter may also be due to the higher acrylonitrile content of the polymer or reduced effectiveness of the modifier which was unchanged from the previous experiment, i.e., 0.45 part of dodecyl mercaptan per 100 parts monomers.

Fractional Precipitation of Polymers Prepared at 30°C.

Three of the polymers were submitted to fractional precipitation from chlorobenzene-methanol solvent-nonsolvent system. The data for the samples are shown in Table II. The gel content of the second sample appears high

TABLE II
SAMPLES FOR FRACTIONATION

Sample	Charge ratio	% Conversion	% Gel	Dilute solution viscosity
T-551-1*	75/25	74.5	—	—
AM-4, 16-5-4	71.5/28.5	68.2	70	3.49
AM-4, 21-6-3	60/40	77.7	49	1.73

* A sample prepared in the Pilot Plant 5-gallon glass lined autoclave.

in view of the high dilute solution viscosity. The integral and differential distribution curves are in Fig. 1. T-551-1 starts to precipitate with 45 volume % methanol content. There is a peak at 45.6 volume % and most of the polymer has precipitated when 46 volume % has been reached. AM-4, 16-5-4 begins to precipitate with 44 volume % methanol, reaches a slightly higher peak at 45 volume % and is largely precipitated with 46 volume %. AM-4, 21-6-3 being of lower viscosity does not start to precipitate until 46 volume % methanol has been reached, a short peak is formed at 47 volume % and the polymer has largely precipitated by 48.5 volume % methanol. Thus the behavior of the polymers was qualitatively similar to that observed in the butadiene-styrene system but the precipitation becomes evident only at high methanol contents of the mixed solvent-nonsolvent, and the molecular weight distribution appears very narrow.

A thorough study of sol-gel equilibrium, swelling index, viscosity, and fractionation curves is required since considerable evidence in the above work was found for strong dependence of some of these variables on solvent to polymer ratio.

Effect of Charge Ratio on the Rate of Conversion at 5°C.

The effect of variation of the butadiene-acrylonitrile charge ratio on the rate of conversion was studied. The data are in Table III and show clearly that 63/37 and 50/50 charge ratios polymerize at the fastest rates. The cause for this optimal rate of conversion will be discussed later.

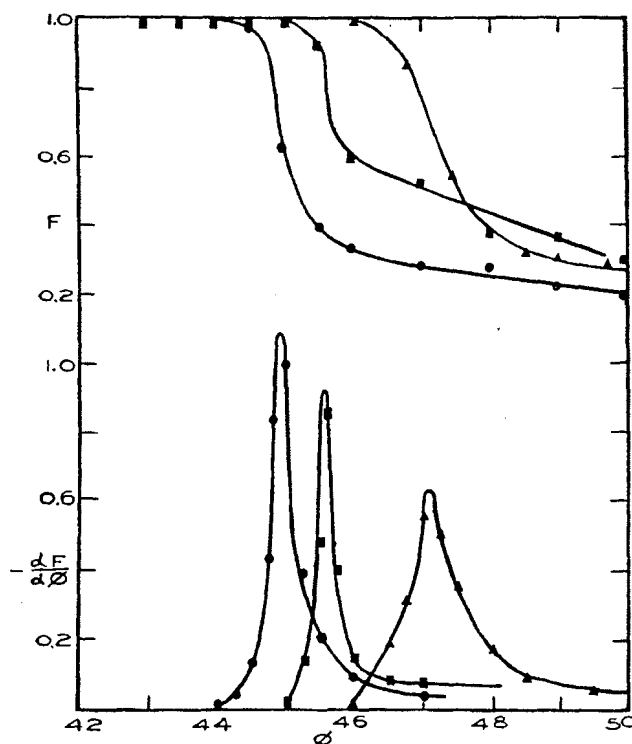


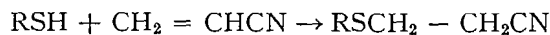
FIG. 1. Fraction of polymer in solution (F) as a function of volume per cent of methanol (ϕ) in chlorobenzene-methanol mixture and differential curves ($-dF/d\phi$) for sample AM-4, 16-5-4 (●), T-551-1 (■) and AM-4, 21-6-3 (▲).

TABLE III
EFFECT OF CHARGE RATIO ON THE RATE OF CONVERSION AT 5°C.

Charge ratio—butadiene/acrylonitrile	% conversion in 17 hr.
75/25	75.8
63/37	96.7
50/50	93.8
25/75	79.0
0/100	0.0

Modifier Disappearance Curves at 5°C.

Some measure of the molecular weight heterogeneity of the polymer may be obtained by measuring the modifier disappearance curves. Titration of the mercaptan was impossible in the normal charge; even without polymerization there appeared to be no residual mercaptan. This was caused by a reaction between the acrylonitrile and the mercaptan (1), whereby the mercaptan was no longer titratable although it still functioned as a modifier or chain transfer agent. This reaction is:



However, this difficulty could be overcome by adding the mercaptan, 0.7 part MTM* per 100 parts monomer, after the acrylonitrile had become diluted with the butadiene and distributed between the two phases. The most convenient method was to add it by syringe and needle to the completed charge optionally in the form of an alcoholic solution. This technique proved adequate to obtain the modifier disappearance data shown in Fig. 2.

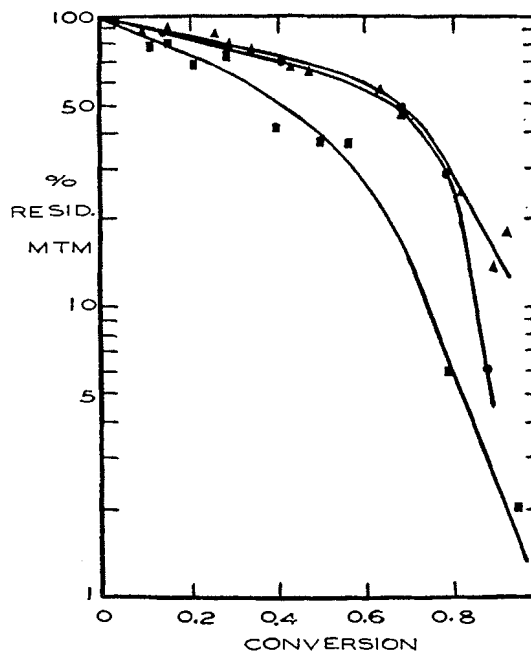


FIG. 2. Modifier disappearance data for mixed tertiary mercaptan blend MTM for 90/10 butadiene/acrylonitrile charge ratio (■), 66/34 charge ratio (●), and 50/50 charge ratio (▲).

It is evident that the rate of disappearance is considerably slower than in butadiene-styrene system (3, 13) and that the rate diminishes with increasing acrylonitrile in the charge. Thus must be interpreted tentatively in terms of a low reactivity of the acrylonitrilyl radical for mercaptan hydrogen. A more comprehensive study of the action of mercaptans as modifiers in this system is to be published (7).

The regulating index, defined as

$$r = \frac{-d \ln R}{dP},$$

where R is the per cent residual mercaptan at fractional conversion P , was calculated for each charge ratio. The results were 1.38 for 90/10, 0.83 for 66/34, and 0.71 for 50/50 charge ratio. These offer a means of numerical comparison with similar calculations in the GR-S and Buna S-3 system (3, 13). There was no waste factor evident in any of the results.

* Phillips Petroleum Co. blend of 60% tertiary C-12, 20% tertiary C-14, and 20% tertiary C-16 mercaptans.

Number Average Molecular Weights

Assuming an average molecular weight for the mercaptan of 220 and that one mercaptan molecule is consumed per molecule of polymer formed, the number average molecular weights based on the data in Fig. 2 were calculated. The results are in Table IV. At low conversions where branching is small and the termination by other than mercaptan is minimal, the results should be reasonably representative.

TABLE IV

NUMBER AVERAGE MOLECULAR WEIGHTS CALCULATED FROM MODIFIER DISAPPEARANCE DATA

% Conv.	90/10 charge ratio		66/34 charge ratio		50/50 charge ratio	
	Mercaptan consumed, %	Molecular weight calc.	Mercaptan consumed, %	Molecular weight calc.	Mercaptan consumed, %	Molecular weight calc.
10	14	2.2×10^4	8	3.9×10^4	8	3.9×10^4
20	25	2.5	14	4.5	14	4.5
30	35	2.7	21	4.5	21	4.5
40	47	2.7	27	4.7	27	4.7
50	61	2.6	33	4.8	37	4.8
60	72	2.6	41	4.6	41	4.6
70	82	2.7	54	4.1	54	4.1
80	94	2.7	74	3.4	71	3.5
90	98	2.9	—	—	84	3.4

These calculations show that the molecular weights of the 90/10 charge ratio polymers are relatively uniform at all conversions and that the molecular weights of 66/34 and 50/50 charge ratio polymers are relatively constant to high conversions at which time the new polymers are of lower molecular weights so that the average is lower. This is shown more clearly by calculating the increment number average molecular weights, Table V, in the same manner. The increment molecular weights for the 90/10 charge ratio remain constant but those for the 66/34 and 50/50 charge ratios decrease above 60% conversion after passing through a broad maximum.

TABLE V

CALCULATED INCREMENT NUMBER AVERAGE MOLECULAR WEIGHTS FROM MODIFIER DISAPPEARANCE DATA

Conversion range	Increment number average molecular weight		
	90/10 charge ratio	66/34 charge ratio	50/50 charge ratio
0-10%	2.2×10^4	3.9×10^4	3.9×10^4
10-20	2.9	5.2	5.2
20-30	3.1	4.5	4.5
30-40	2.6	5.2	5.2
40-50	2.2	5.2	5.2
50-60	2.9	3.9	3.9
60-70	3.1	2.4	2.4
70-80	2.6	1.6	1.8
80-90	7.8	—	2.4

Dilute Solution Viscosity of Polymers Prepared at 5°C.

Another means of measuring molecular weight heterogeneity is by following the dilute solution viscosity of the polymer at various conversions. The viscosity changes with 75/25 and 66/34 charge ratios are shown in Fig. 3. It will be noted that with fresh latex the viscosity increases regularly with conversion but after the latex is aged the viscosity of the initial polymer has increased and that of the higher conversion samples has remained constant. The absence of a maximum as shown in Table I may be attributed to the larger amount of mercaptan present or to the lower polymerization temperature. Previous work (23) appears to have been done on aged latex. Similar data were collected for 50/50 and 25/75 butadiene to acrylonitrile charge ratio and are in Fig. 4. The viscosity increases to a maximum and then decreases for the 50/50 charge ratio. The decrease may be due to the increased rate of mercaptan disappearance at higher conversion together with the reduced tendency for branching of the substantially vinyl polymer. It seems that the dimethylformamide solvent consistently yields lower results than dichlorobenzene-isopropanol mixture. Again the viscosity of the aged latex has changed in the lower conversion ranges but has not increased above that of unaged latex in the higher conversion ranges. The few data with the 25/75 charge ratio indicate a regular decrease in viscosity which might be expected from the increasing acrylonitrile content of the polymer in addition to changes in the modifier disappearance curve and the reduced chances of branching.

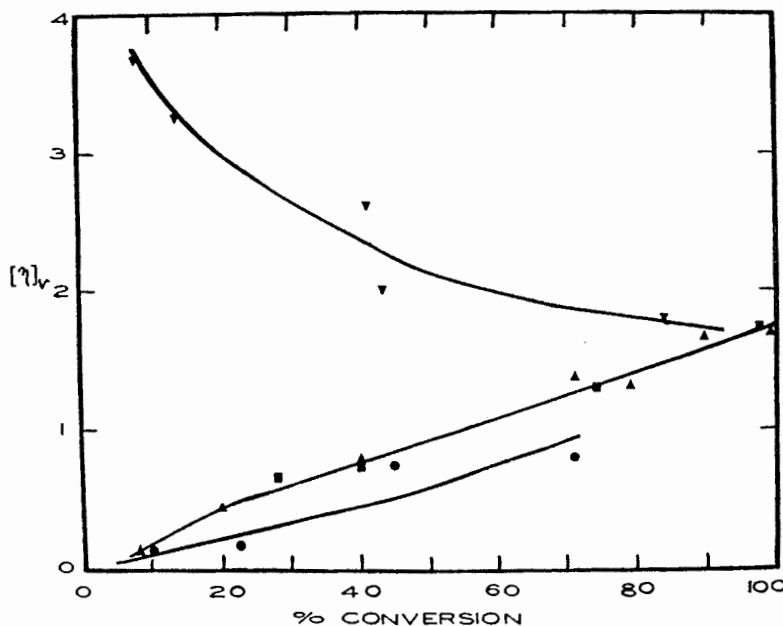


FIG. 3. Viscosity conversion curves. 75/25 butadiene/acrylonitrile charge ratio in benzene-isopropanol (●); 66/34 same (■); 66/34 in *o*-dichlorobenzene-isopropanol (▲), same after two months (▼).

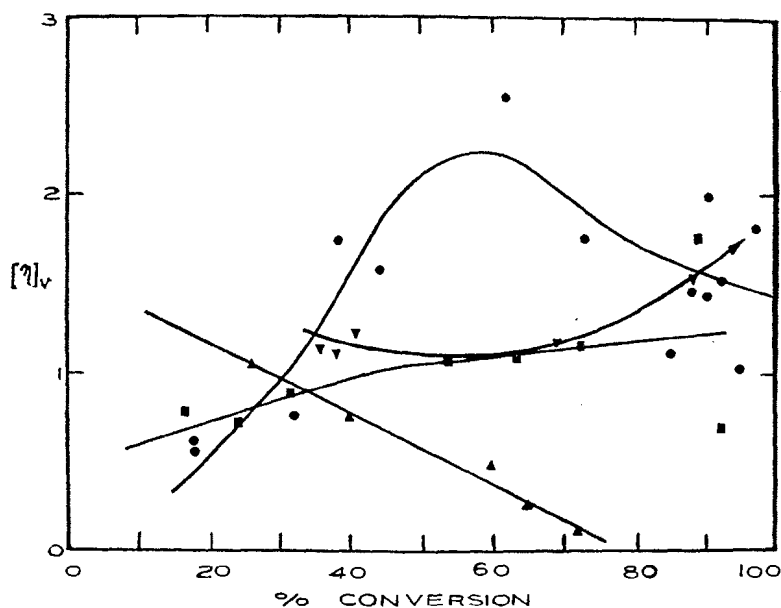


FIG. 4. Viscosity conversion curves. 50/50 butadiene/acrylonitrile charge ratio in dichlorobenzene-isopropanol (●); same in dimethylformamide (■); same after two months (▼); 25/75 charge ratio in same (▲).

The increment viscosity may be calculated from the viscosity conversion data. The increment viscosity is that which will change the viscosity of the whole polymer from the value at the beginning of the range to the value at the end of the range. The data are in Table VI. The increment viscosity for the 75/25 and 66/34 ratios increases regularly, for the 50/50 charge ratio rapidly and then diminishes, and for the 25/75 ratio diminishes regularly.

Viscosity Molecular Weights

Conversion of the viscosity data into molecular weights can be made by using a Staudinger type equation. Almost any arbitrary equation would

TABLE VI
CALCULATED INCREMENT VISCOSITY FROM VISCOSITY-CONVERSION DATA

Conversion range	75/25 charge ratio	66/34	50/50	25/75
	Increment viscosity			
10-20%	0.32	0.68	—	—
20-30	0.68	0.95	1.83	0.55
30-40	0.68	1.28	3.31	0.15
40-50	1.05	1.57	4.54	—ve
50-60	1.57	1.92	2.50	—ve
60-70	2.14	2.18	0.80	—ve
70-80	—	2.61	0	—
80-90	—	2.82	0	—
90-100	—	3.33	0	—

suffice for relative values. One applicable in this work has been published (18). The difference between the data for benzene and toluene solution is not sufficient to exclude the use of the equation for toluene solution when benzene or dichlorobenzene is the solvent. The intrinsic viscosities in all these solvents appear to be nearly identical in practice as shown in part of Fig. 3. The equation is $\eta = 4.9 \times 10^{-4} M^{0.64}$. This was used to calculate the molecular weight versus conversion, Table VII. The increment viscosity molecular weights were calculated likewise and are in Table VIII.

TABLE VII
CALCULATED VISCOSITY AVERAGE MOLECULAR WEIGHTS

% Conversion	75/25 charge ratio	66/34 charge ratio	50/50 charge ratio	25/75 charge ratio
10	$< 1 \times 10^4$	$< 1 \times 10^4$	—	—
20	1.5	4.5	6.9×10^4	24.0×10^4
30	3.0	8.0	18.5	18.5
40	4.9	12.5	34.0	12.5
50	7.8	17.8	45.0	6.9
60	12.0	21.8	48.0	3.1
70	17.5	24.5	43.0	< 1
80	—	29.5	38.0	—
90	—	34.5	34.5	—
100	—	37.5	29.5	—

TABLE VIII
CALCULATED INCREMENT VISCOSITY MOLECULAR WEIGHTS

Conversion range	75/25 charge ratio	66/34 charge ratio	50/50 charge ratio	25/75 charge ratio
10-20	2.8×10^4	7.8×10^4	—	—
20-30	7.8	18	3.9×10^4	7.2×10^4
30-40	7.8	27	66	21
40-50	21	34	84	-ve
50-60	34	40	53	-ve
60-70	46	46	14	-ve
70-80	—	58	0	—
80-90	—	58	0	—
90-100	—	66	0	—

Heterogeneity of Polymers

Having both the number average molecular weights and the viscosity average molecular weights it is possible to estimate the heterogeneity of the polymer (8, 16). From the relationships and the viscosity molecular weight equation it can be derived (following the suggestion of Meehan*) that

$$\beta = 2.37 \sqrt{\log R} \text{ and } M_0 = \bar{M}_n R^{-0.610},$$

where R is \bar{M}_v/\bar{M}_n . Using the above values, β and M_0 were calculated for

* Private communication to participants in The Rubber Reserve research program.

the 66/34 and 50/50 charge ratios. The data are in Table IX. For both ratios the heterogeneity increases with conversion, and the peak of the distribution curve shifts to lower molecular weights.

TABLE IX
CALCULATION OF THE HETEROGENEITY AND PROBABLE MAXIMUM IN THE DISTRIBUTION CURVE OF MOLECULAR WEIGHTS

% Conversion	66/34 charge ratio		50/50 charge ratio	
	β	M_0	β	M_0
10	-ve	9.4×10^4	—	—
20	0	4.5	0.47	3.4×10^4
30	0.59	3.2	1.46	1.9
40	1.12	2.4	2.04	1.4
50	1.35	2.2	2.30	1.2
60	1.60	2.0	2.41	1.1
70	1.84	1.4	2.42	1.0
80	2.22	0.9	2.46	0.8
90	—	—	2.38	0.8

In a similar manner the heterogeneity and the peak of the distribution curve for the increment polymer can be calculated, and the data are in Table X. The form of the curves is similar although the heterogeneity of the 50/50 ratio copolymer seems to be diminishing with increasing conversion. This again occurs when polymer of lower molecular weight is formed.

From these calculated curves the usual derived data can be obtained. These include the percentage of polymer having various characteristics, etc. In general the values of β and M_0 are sufficient to visualize the approximate molecular weight distribution of the polymers, and the data show that the system behaves much like GR-S or Buna S-3 (3) except as will be shown later when polymer rich in acrylonitrile is formed.

Bound Acrylonitrile versus Conversion

In addition to molecular weight heterogeneity there is chemical heterogeneity along the chain. One aspect of this problem which can be studied is

TABLE X
CALCULATION OF HETEROGENEITY AND PROBABLE MAXIMUM IN THE DISTRIBUTION CURVE OF MOLECULAR WEIGHTS FOR THE INCREMENT POLYMER

Conversion range	66/34 charge ratio		50/50 charge ratio	
	β	M_0	β	M_0
10-20	1.0	4.1×10^4	—	—
20-30	1.8	1.9	2.2	1.3×10^4
30-40	2.0	1.9	3.9	1.1
40-50	2.1	1.6	2.6	1.0
50-60	2.4	0.9	2.4	1.0
60-70	2.7	0.4	1.8	1.1
70-80	2.9	0.2	—	—

the variation of bound acrylonitrile with conversion. The results for the 75/25 butadiene/acrylonitrile charge ratio are in Fig. 5. The bound acrylonitrile values were determined experimentally and used to calculate the increment acrylonitrile. This is the acrylonitrile content of the polymer being produced over a narrow range near the conversion indicated. Also the bound acrylonitrile was used to calculate the charge ratio of the residual monomers which would be expected to be related to the increment acrylonitrile through the reactivity ratios of the respective monomers. It is evident that the bound acrylonitrile is higher in the initial polymer than it is in the charge ratio and that polymer increasingly rich in butadiene is formed during the reaction to bring the final average polymer to a bound acrylonitrile equivalent to the charge ratio. During the reaction also the percentage of butadiene in the residual monomers increases.

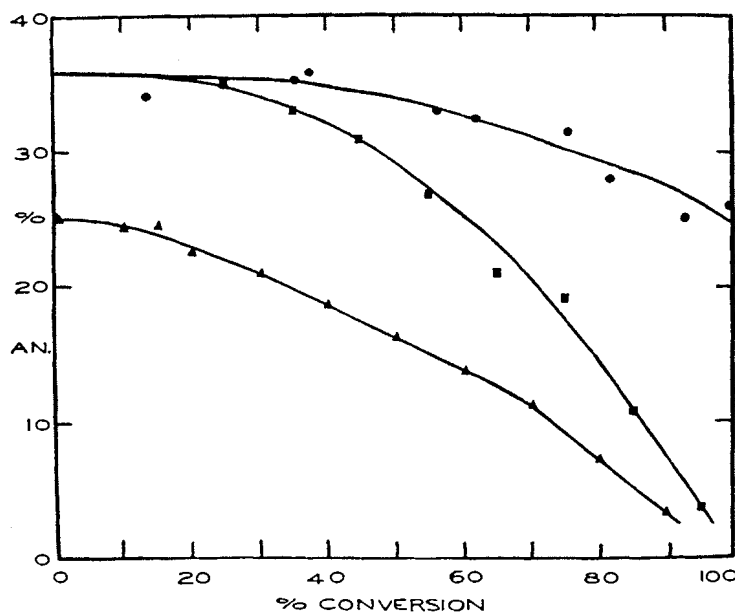


FIG. 5. Acrylonitrile versus conversion for 75/25 butadiene/acrylonitrile charge ratio. (●) in polymer, (■) in increment polymer, (▲) in residual monomer.

A different picture is observed when the 50/50 butadiene/acrylonitrile charge ratio is used, Fig. 6. These data show that the polymer formed is remarkably uniform chemically to 90% conversion after which there is a short period in which acrylonitrile content in the polymer formed rises steeply. The residual charge ratio increases slowly at first and then more rapidly until it appears as if all the butadiene is exhausted near the end of the reaction.

Still a different picture is evident from the 25/75 butadiene/acrylonitrile charge ratio, Fig. 7. In this case the bound acrylonitrile starts at a value much lower than the charge ratio and increases slowly at first and then rapidly until the final average is equivalent to the charge ratio. The increment

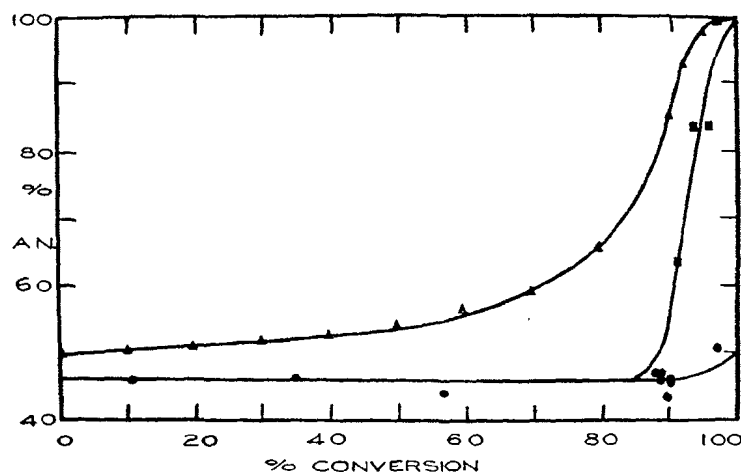


FIG. 6. Acrylonitrile versus conversion for 50/50 butadiene/acrylonitrile charge ratio. (●) in polymer, (■) in increment polymer, (▲) in residual monomer.

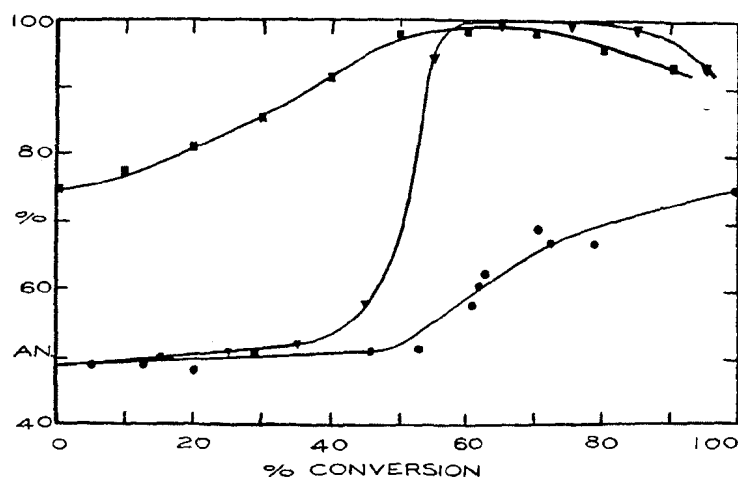


FIG. 7. Acrylonitrile versus conversion for 25/75 butadiene/acrylonitrile charge ratio. (●) in polymer, (▼) in increment polymer, (■) in residual monomer.

acrylonitrile likewise increases slowly at first and then rapidly. It attains the impossible values of slightly over 100%, which indicates that the slope of the bound acrylonitrile curve is changing too rapidly probably through an analytical error. Not only are bound acrylonitrile analyses difficult in this region but also the latex suddenly forms a suspengel which must be sampled by breaking the bottle and chipping off a portion of the spongy mass. This is an uncertain way of obtaining a representative sample. Also the mechanism of formation of this suspengel may be such that abnormal bound acrylonitrile values would result. This same error appears naturally in the residual charge ratio which indicates the disappearance of butadiene and its later reappearance. Both anomalies can be removed by slight changes in the original bound acrylo-

nitrile curves. Similar anomalies were observed in systems rich in styrene (13) although the deviations were less pronounced and were definitely due to analytical errors in the region investigated.

Reactivity Ratios of the Monomers, Q and e

By extrapolating the bound acrylonitrile versus conversion curve to zero conversion an estimate of the reactivity ratio r_1 and r_2 (where r_1 is the ratio of the rate of reaction of butadienyl radical with butadiene to the rate of reaction of butadienyl radical with acrylonitrile and r_2 is the ratio of the rate of reaction of acrylonitryl radical with acrylonitrile to the rate of reaction of acrylonitryl radical with butadiene) may be made by the linear method (2). The results are $r_1 = 0.29$ and $r_2 = 0.02$. The value of r_1 is lower than the previously tabulated results (24) owing to the wider molar ratios used and possibly to the method of calculation which eliminates the undue weighting of the results obtained with small amounts of acrylonitrile in the charge. The value of r_2 reported earlier (24) was -0.1 , which was meaningless. The present value of $r_2 = 0.02$ seems to fit the experimental results satisfactorily.

It is interesting to plot the per cent acrylonitrile in the charge against the per cent acrylonitrile in the initial polymer formed. In this way an S-shaped curve is obtained, Fig. 8, in which the points are from Figs. 5, 6, and 7, and the curve is the theoretical for $r_1 = 0.29$ and $r_2 = 0.02$ in the equation

$$\frac{dB}{dA} = \left(\frac{B}{A}\right) \left(\frac{r_1 \left(\frac{B}{A}\right) + 1}{\left(\frac{B}{A}\right) + r_2} \right),$$

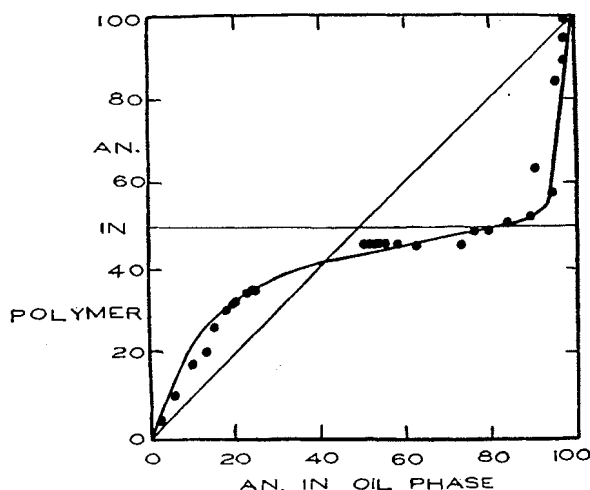


FIG. 8. Acrylonitrile in polymer versus acrylonitrile in charge. (•) data from Figs. 5, 6, and 7. Curve theoretical for $r_1 = 0.29$ and $r_2 = 0.02$.

in which $\frac{B}{A}$ is the molar ratio of butadiene to acrylonitrile in the monomers and $\frac{dB}{dA}$ is the molar ratio of butadiene to acrylonitrile in the polymer being formed. For convenience these were calculated in terms of per cent acrylonitrile. The closeness of the agreement is satisfactory except for the charges very low in acrylonitrile. Were the copolymerization random, the result would be a straight line connecting zero and 100%. With butadiene and acrylonitrile, the polymer formed when less than 44% acrylonitrile is in the charge is richer in acrylonitrile than is the charge ratio, whereas if the acrylonitrile in the charge is greater than 44% the acrylonitrile in the polymer is less than in the charge ratio. This illustrates the strong tendency for butadiene and acrylonitrile to alternate in the chain, an effect which will be discussed later in more detail.

The data of Smith (21) may be used to calculate the distribution of acrylonitrile between an oil phase and water, assuming that the oil phase behaves similarly to styrene. This may not be true but until a satisfactory study* of the partition of acrylonitrile between butadiene and water is available the data (21) are at least an approximation. The calculated values used in the study are in Table XI.

TABLE XI
CALCULATION PERCENTAGE OF THE ACRYLONITRILE IN THE OIL PHASE

Butadiene/acrylonitrile charge ratio	Acrylonitrile % in oil phase
90/10	56
80/20	62
70/30	65
60/40	69
50/50	71
40/60	72
30/70	73
20/80	74
10/90	75
0/100	76

Recalculating the results in Figs. 5, 6, and 7 on this basis yields values of $r_1 = 0.18$ and $r_2 = 0.03$. Plotting the data in Fig. 9 shows that now the experimental results are close to the theoretical curve for $r_1 = 0.18$ and $r_2 = 0.03$ all along the line. At least a satisfactory approximation has been achieved.

* A preliminary study of the distribution of acrylonitrile between butadiene and water suggests that under the experimental conditions used in this paper 87%, 92%, and 94% of the acrylonitrile is in the oil phase for 75/25, 50/50, and 25/75 butadiene/acrylonitrile charge ratio respectively. These results applied to Figs. 5, 6, and 7 yield $r_1 = 0.24$ and $r_2 = 0.03$. Such data would yield points and a theoretical curve similar to but intermediate between those of Figs. 8 and 9.

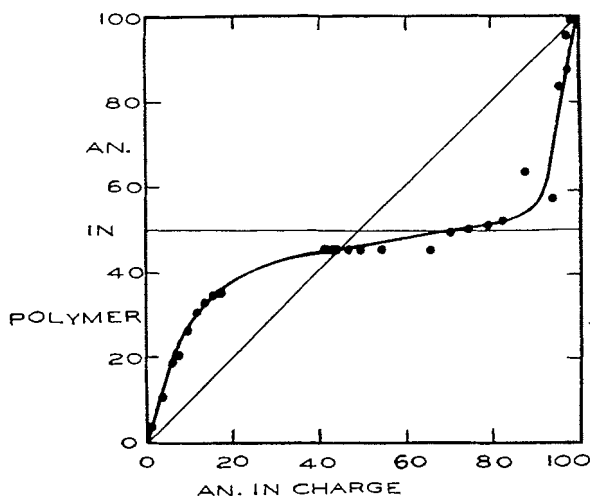


FIG. 9. Acrylonitrile in polymer versus acrylonitrile in oil phase of charge. (•) data from Figs. 5, 6, and 7 as changed by Table XI. Curve theoretical for $r_1 = 0.18$ and $r_2 = 0.03$.

Discussion

A general comparison of interest is the increment acrylonitrile curves. A series has been published by Semon (19, 20). His results showed that 62.6/37.4 mole ratio of butadiene to acrylonitrile was azeotropic, i.e., the polymer was of constant composition throughout. Also his data showed that when the charge ratio varied from 56/44 to 77/23 the initial polymer formed varied from 1.5/1 to 2/1 mole ratio of butadiene to acrylonitrile. The experimental data above are qualitatively similar but suggest an azeotropic mixture containing a higher acrylonitrile proportion. The exact value would seem to be a fortuitous balance between reactivity ratio, distribution of monomers between phases, and perhaps other factors, and it would be surprising if these could be balanced exactly to 100% conversion. Also the data above suggest that the initial polymer produced at 5°C. is richer in acrylonitrile than for the corresponding charge ratio at higher temperatures since the mole ratio of the initial polymer when the charge ratio is varied from 25/75 to 75/25 varies from 1/1 to 1.75/1 mole ratio butadiene to acrylonitrile, i.e., lower than at the higher polymerization temperature. This may be due to lower solubility of acrylonitrile in water at the lower temperatures. The azeotropic charge ratio from Fig. 9 would appear to be 54/46 butadiene/acrylonitrile for bulk phase polymerization. Comparison with similar curves for the styrene-acrylonitrile system (21) shows the more flattened central portion of the curve and the shift upwards of the azeotropic concentration of the above data.

The dilute solution viscosity indicates that the molecular weight increases usually regularly but in the case of the 50/50 ratio to a maximum and then decreases and in the case of the 25/75 ratio polymer decreases regularly. In the former the changed direction of the trend coincides with the formation of

low molecular weight polymer owing to increased rate of disappearance of the mercaptan, and in the latter to this effect and the formation of polymer richer than 50% in bound acrylonitrile. The high acrylonitrile polymer seems to behave in a different fashion from the less rich copolymer in the same solvent, perhaps in a manner similar to a polyelectrolyte but under the influence of those forces associated with the oil resistance of this type of polymer.

The relationship between viscosity and molecular weight is sufficiently close to be of suitable use for calculation of approximate viscometric molecular weights. These compared with the number average molecular weights yield some indication of the probable maximum of the molecular weight distribution and the heterogeneity of the various polymers. Since a number of effects have to be considered negligible the results can be in considerable percentage error but probably little relative error. In general as the conversion increases the heterogeneity becomes greater and the probable maximum in the distribution curve occurs at lower molecular weights. However, when the viscosity curve reverses direction with the formation of low molecular weight polymer the relationships again do not follow the expected pattern, i.e., the heterogeneity passes through a maximum and the peak of the distribution curve remains relatively constant. The data obtained when polymer containing over 50% acrylonitrile is formed are difficult to interpret as yet.

It will be noted that in copolymerizations with butadiene or styrene with acrylonitrile (11) there is a greater tendency for these monomers to form a radical more reactive towards acrylonitrile than to themselves, whereas acrylonitrile also forms a radical and more reactive towards butadiene or styrene than to acrylonitrile. Such a situation would cause the polymer chain to tend to alternate between acrylonitrile and butadiene or styrene. Thus the rate of polymerization is greatest for approximately equal molar ratios. This also leads to a small value of the $r_1 \cdot r_2$ product (10) which is considered a measure of the alternating tendency. Price (17) has used such data also to compute a value Q and a value e , the former to represent the average reactivity of the double bond and the latter to represent a measure of the polarity of the complex. The Q and e for acrylonitrile in the butadiene-acrylonitrile system appear to be 0.74 and 1.47 respectively. The values are appreciably higher than those recorded (see (11)) owing to the greater tendency of butadiene and acrylonitrile to alternate under the conditions of these experiments. This has been observed for the butadiene-styrene system (16). Further investigation under more varied conditions is needed to ascertain whether such effects are real.

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