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Acrylonitrile Copolymerizations. IV. Butadiene Copolymerization

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SUMMARY

The kinetics of the acrylonitrile–butadiene radical copolymerization, carried out in solution at 60°C, have been followed using gas chromatographic analysis. Remote units effects are observed only on the butadiene-ended radicals but they seem to involve a quite long sequence of butadiene units. The following values of the reactivity ratios are proposed: $r_A = 0.067$, $r_{AB} = 0.70$, $r_{ABB} = 0.66$, $r_{ABBB} = 0.17$, $r_{Bi} \rightarrow 0.01$ to 0.06 for large values of i . The results are discussed in terms of either polarity effects, or differences in reactivities between 1,4- or 1,2-butadiene radicals, or finally of charge transfer complexes between the monomers.

Only a few studies have been published about the kinetics of the radical copolymerization of acrylonitrile (A) and butadiene (B). From Table 1 it may be seen that the reactivity ratios determined do not agree well [1-4]. Also, the experiments have been carried out on a limited range of monomer feed composition.

The experimental techniques based on gas chromatographic analysis developed in our laboratory [5] allow us to present more precise results which cover the whole range of monomer feed composition.

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Table 1. Literature Data

r_B	r_A	T (°C)	Experimental conditions	Range $x_B = B/A$	Copolymer Analysis	Refs.
0.29	0.02	5	Emulsion	0.11-10.0	N	1
0.18	0.03	5	Bulk	0.11-10.0	N	1
0.35	0.00	50	Bulk (0.1%BP) ^a	-	-	2
0.40	0.04	50	Bulk (TIBB) ^b or emulsion	0.11-4.0	N	3
0.33	0.25	60	-	-	-	4

^aBP = benzoyl peroxide.

^bTIBB = triisobutylboron.

EXPERIMENTAL

The copolymerization initiated by azobisisobutyronitrile (0.01 mole/mole of monomer) were carried out at 60°C in dimethylformamide solution. The feeds of the reactor are given in the Table 2 together with the kinetics results deduced from gas chromatographic analysis using the solvent as internal concentration reference. Larger samples were picked up at limited conversion (less than 10%) and the polymers, isolated through precipitation, washing, and drying, were studied by IR spectroscopy (Perkin-Elmer 125) as films or KBr pellets, and also by NMR spectroscopy (Varian DA-60-IL) in concentrated solution (10%) in d_6 -benzene or d_7 -dimethylformamide.

RESULTS

The Fineman-Ross [6] plot of our results, together with those given by Ashikari [3] which seem to be the most reliable literature data, is illustrated by Fig. 1. It may be seen that a linear plot is obtained only for the monomer feed rich in A ($x_B = B/A < 1$). From this plot one obtains $r_B = 0.58$ and $r_A = 0.067$. These values agree with those of Ashikari. Also the linear plot fits very well with the results for mixtures extremely rich in A. It may be safely concluded that only one reactivity ratio is sufficient to describe the reactivity of the A-ended radicals. On the other hand, the

Table 2. Charge and Chromatographic Kinetic Results in the Acrylonitrile (A)–Butadiene (B) Copolymerization

B (moles)	A (moles)	Solvent DMF (Mole)	$x_B = B/A$	$n_B = dB/dA$
0.974	0.0185	4.99	52.6	5.9
0.990	0.0306	4.45	32.2	5.2
0.974	0.0483	5.33	20.2	4.5
1.150	0.1130	5.46	10.2	3.7
1.210	0.1435	4.82	8.40	3.47
1.210	0.187	4.81	6.45	3.23
0.334	0.963	4.89	0.346	1.01
0.143	0.985	5.47	0.145	0.74
0.0907	1.005	5.56	0.0908	0.625
0.0344	0.996	4.45	0.0345	0.345

departure observed for the values of $x_B > 1$ indicate the existence of a penultimate effect. In this hypothesis, the copolymer equation is

$$n = \frac{1 + \frac{r_{AB}x(1 + r_{BB}x)}{1 + r_{AB}x}}{1 + r_A/x}$$

where $n = dB/dA$.

A plot of

$$\frac{n(1 + r_A/x) - 2}{x} \text{ vs. } \frac{n(1 + r_A/x) - 1}{x^2}$$

is expected to give a straight line which gives r_{BB} from the intercept and r_{AB} from the slope. Such a plot is illustrated by Fig. 2. A straight line fits well the results for $x_B < 4$, which gives $r_{AB} = 0.70$ and $r_{BB} = 0.30$. However, a departure is again observed when the amount of butadiene is greater than 80%.

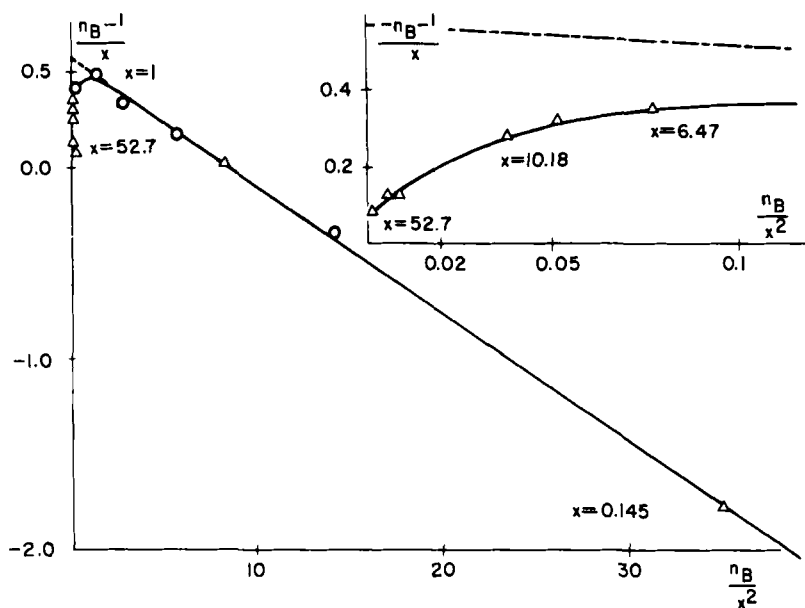


Fig. 1. Terminal effect, Fineman-Ross plot. (○) Ashikari [3]; (△) this study.

Using the equation proposed by Ham [7] and a procedure previously described by us [8], it is possible to derive the values of the reactivity ratios corresponding to antepenultimate effects upon the B-ended radicals. The plot of the linearized form of the Ham equation, assuming $r_A = 0.07$ and $r_{AAB} = r_{BAB} = 0.7$, is illustrated by Fig. 3. The experimental data for $x_B < 11$ fit well a straight line from which one obtains $r_{BBB} = 0.17$ and $r_{ABB} = 0.66$. These values, in turn, permit the determination of $r_{AAB} = 0.80$ and $r_{BAB} = 0.77$. Using these values in the first equation does not significantly change the values of r_{BBB} and r_{ABB} .

The above procedure bears two kinds of weakness. First, it does not take account of the copolymer containing more than 90% butadiene, and second, the Ham equation used to obtain r_{AAB} and r_{BAB} is not correct. A correct equation, first derived by Price [9] and later by Ito and Yamashita [10], cannot be used in a linearized form, so that the unique determination of the reactivity ratios is not possible. However, it may be noted that there is no penultimate effect onto A radical, and apparently no antepenultimate effect onto an AB radical. Thus it may be assumed

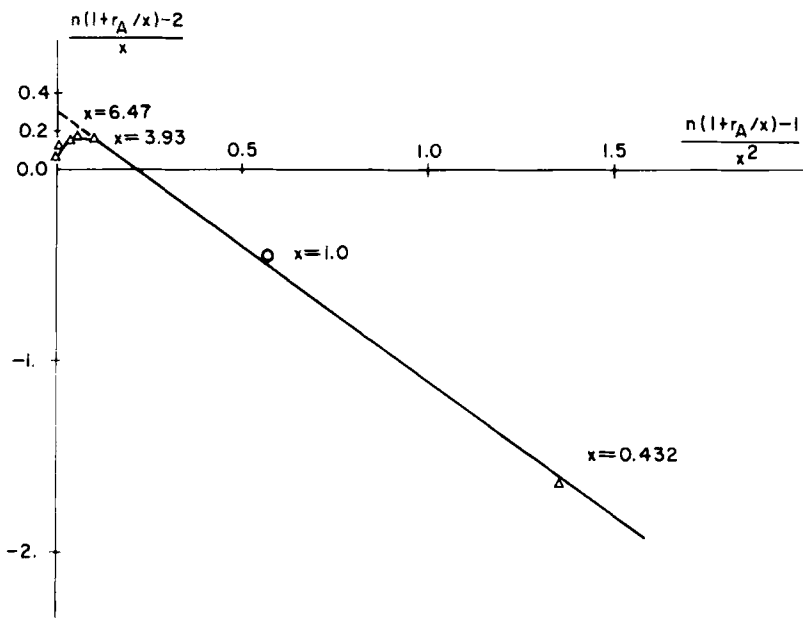


Fig. 2. Penultimate effect, Fineman-Ross plot. (O) Ashikari [3]; (Δ) this study.

that the rule is general and that remote units effects are to be considered only for radicals ended by a sequence of B units. Further it may be noted that, for the copolymers with high butadiene contents, the A units are chiefly isolated and that AA diads or longer A sequences are practically absent.

Based on this hypothesis, the correct Price equation is greatly simplified and becomes identical to the Ham equation, so that the procedure of linearization may be extended to the next step of ante-antepenultimate effect. The next equation is easily obtained as

$$\frac{N - 2}{x} = r_{BBBB} - \frac{N - 1}{x^2} \frac{1}{r_{ABBB}}$$

where

$$N = \left\{ [n(1 + r_A/x) - 1] \left(1 + \frac{1}{r_{AB^x}} \right) - 1 \right\} \left(1 + \frac{1}{r_{ABB^x}} \right)$$

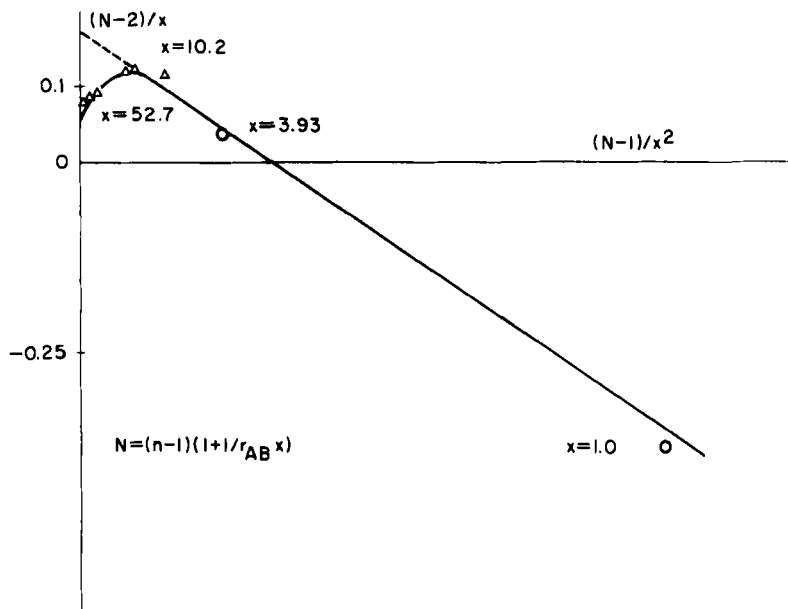


Fig. 3. Antepenultimate effect, Fineman-Ross plot. (O) Ashikari [3]; (Δ) this study.

From the plot of $(N - 2)/x$ vs. $(N - 1)/x^2$, one obtains $r_{BBBB} = 0.06$ and $r_{ABBB} = 0.27$. The straight line fits the experimental results up to $x = 30$. Possibly the above procedure might be extended to another step of remote unit effect for larger values of x . It may be easily shown also that the limiting value of r_{Bi} for large i when x increases indefinitely is given by the intercept of a plot of n/x vs. $1/x$. The value may be estimated between 0.01 and 0.06.

DISCUSSION

The interpretation of the above results is rather difficult. What might be the cause of such large remote unit effects?

It may be observed at first that the situation is not very different from that of the styrene-acrylonitrile copolymerization where antepenultimate effects have been observed on the styrene-ended radicals [17], but in that case these effects were sufficient to fit the kinetic results and it was not

necessary to involve the effects of more remote units. In this connection the difference in polarity between acrylonitrile and the second monomer is the largest in the case of butadiene as shown by the values of e in the Q-e scheme: ($e_B = -1.05$ and $e_S = -0.8$). If the remote effects are caused by the polarity of the monomer units, it is necessary to admit that the inductive effects of the substituent groups may operate through two σ -bonds so that one has to admit that some conjugation does remain between the π -electrons of two successive 1,4-butadiene units. Such a conjugation must be broken either by an acrylonitrile unit or by a 1,2-butadiene unit. If such an assumption has some validity, it raises the question of the comparative reactivities of the radicals carried by a 1,2- or 1,4-unit. In turn, it might be possible to involve a difference in reactivity in order to explain the departure of the composition, Δn , from the one, n_c , calculated for the terminal model (Fineman-Ross plots in Fig. 1).

Table 3

x_B	P_B	52.7	32.4	20.2	10.2	6.47	3.93	1.0	
$\Delta n/n_c$	—	0.85	0.75	0.67	0.43	0.27	0.11	0.0	
1-2% (IR spectra)		21.0	21.0	19.3	18.8	15.5	12.4	11.5	10.0

This might be supported by a comparison (Table 3) of $\Delta n/n_c$ with the per cent of 1,2-units in polybutadiene as determined from the infrared spectra, following the method proposed by Morero et al. [11]. This method, however, may not be applied safely to the present copolymers. Further, it seems to be highly imprecise if the amount of acrylonitrile in the copolymer is high. A study by NMR spectroscopy, described in detail elsewhere [12], shows that the amount of 1,2-units is a linear function of the butadiene content and varies between 0 and 25% when the copolymer is varied from pure acrylonitrile to pure polybutadiene. It thus may be concluded that the addition of a butadiene unit to an A radical takes place exclusively in the 1,4-configuration. As shown in the Appendix, which gives an example of kinetic interpretation taking into account the difference between the $B_{1,4}$ (B_4) and $B_{1,2}$ (B_2) radicals, this fact necessarily implies the occurrence of a penultimate effect on a B_4 radical. However, the calculation developed in the Appendix also shows that the introduction of the two kinds of B radicals does not change the nature of the com-

position equation fundamentally. So assuming four different kinds of radicals; A^* , AB_4^* (or A_4), BB_4^* (B_4), and BB_2^* (B_2), we obtain an equation (Eq. 14 in the Appendix) which may be plotted as in Fig. 2 giving

$$r_{BB} = 0.30 = 4r_A \frac{1 + r_2}{r_2} \frac{1}{1 + r_{A_4 2}}$$

and

$$r_{AB} = 0.70 = r_{A_4 A} \frac{1 + r_{A_4 2}}{r_{A_4 2}}$$

where the various reactivity ratios are defined in the Appendix. From a study of the microstructure it is possible to obtain $r_{A_4 A} = 0.37$ and $r_{A_4 2} = 1.1$, which compare the reactivities of the AB_4^* radical versus the 1,2-butadiene or the acrylonitrile addition.

The complete solution of the problem is, however, very complex and initially involves more information about the butadiene homopolymerization, which is expected to be obtained from a study of the sequence distribution. It is also probably necessary to introduce the remote unit effect of the 1,2-addition in the homopolymerization and copolymerization of butadiene.

Finally, another reaction might explain the composition; namely, the Diels-Alder adduct between butadiene and acrylonitrile to give cyano-3-cyclohexene. This reaction has been already described for temperatures above 80°C [13-15]. In fact, we have observed from gas chromatographic analysis that, at above 100°C , cyanocyclohexene and vinyl-3-cyclohexene are formed in comparable amount, but during polymerization at 60°C only traces of these products are obtained in the extreme range of the monomer feed composition. In the intermediate range these products may together account for a maximum of 1% of the monomer consumption.

However, the formation of this adduct might lead to a better explanation of the observed effects. As recently suggested by Gaylord [16], the adduct is formed through a charge transfer complex between the two monomers which is activated thermally. But the activation of this charge transfer complex may also be done by radicals and then lead to copolymerization. Gaylord has shown that the copolymerization of a charge transfer complex between maleic anhydride and dienes is very rapid. In the butadiene-acrylonitrile case, two charge transfer complexes are possible between

one butadiene and one acrylonitrile molecules (complex AB) or between two butadiene molecules (complex BB). In both cases one butadiene molecule is in a 1,4-configuration. In the latter case the second butadiene molecule is probably in the vinyl configuration because the structure of the adduct is vinyl-3-cyclohexene. Thus when a BB complex copolymerizes it gives a B_4 - B_2 sequence. This may explain the rather high value of r_{A42} and the rather high content of B_2 units at low butadiene content, given the fact that the acrylonitrile does add the butadiene in the B_4 configuration. On the other hand, the reason for this selective AB_4 sequence might be the participation of the AB complex. Finally, it is easy to show that the proportion of A monomer in the AB complex is higher when the A content of the monomer feed is lower; thus if the reactivity of the AB complex is much higher than that of the monomers, the relative consumption of the A monomer would be the greatest in the same part of the range, just as observed experimentally.

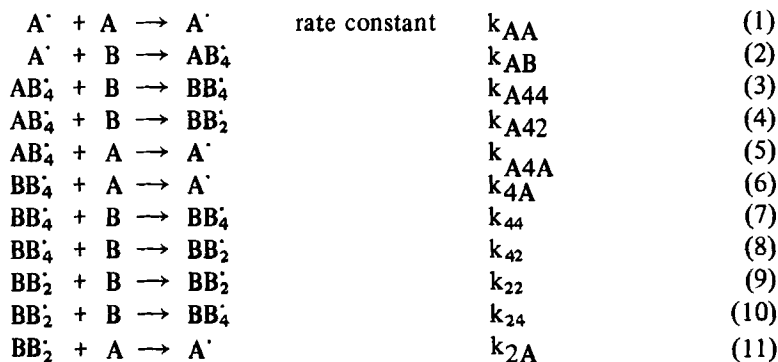
We may conclude that the participation of charge transfer complexes between monomers in the copolymerization process gives a good explanation of the observed effects. This explanation is also valid for the styrene-acrylonitrile case, although the concentration of complexes is probably lower. Such an explanation has been proposed recently by Litt and Seiner [18] for other cases where penultimate effects would be suspected. In any event, much work remains to be done in order to understand these phenomena.

APPENDIX

Derivation of a Composition Equation Taking in Account Different Reactivities for the Butadiene 1,2- and 1,4-Radicals

It was first assumed that no penultimate effects were operative, but the derivation of the copolymerization equation led to an equation very similar to that of Lewis and Mayo, giving a theoretical straight line in a Fineman-Ross plot.

Thus we considered the four different radicals A^{\cdot} , AB_4^{\cdot} , BB_4^{\cdot} , and BB_2^{\cdot} , assuming that a penultimate effect was operative only on the B_4 -ended radical. The following propagation reactions were considered:



We define the following reactivity ratios which must be determined as

$$r_A = \frac{k_{AA}}{k_{AB}}, r_{A4A} = \frac{k_{A44}}{k_{A4A}}, r_{A42} = \frac{k_{A44}}{k_{A42}}, r_{4A} = \frac{k_{44}}{k_{4A}}, r_{2A} = \frac{k_{22}}{k_{2A}},$$

$$r_4 = \frac{k_{44}}{k_{42}}, r_2 = \frac{k_{22}}{k_{24}}$$

From the steady-state assumption applied to the four radicals and also to the two radicals present in the homopolymerization of butadiene, it is possible to derive the various ratios of the radicals concentrations and also to obtain the relation

$$r_{A42}r_2r_{4A} = r_{2A}r_4 \quad (12)$$

Also, from the composition of the pure polybutadiene (25% 1,2 and 75% 1,4), we have

$$r_4 = 3r_2 + 2 \quad (13)$$

Then, upon calculation of dA/dt , dB/dt , and finally $dB/dA = n$, the final copolymerization equation is obtained, taking in account Eqs. (12) and (13)

$$\frac{dB}{dA} = n = \frac{1 + 4r_{2A}(1 + r_2)/r_2(1 + r_{A42})}{1 + r_{A42}/(1 + r_{A42})r_{A4A}^x} \quad (14)$$

$$1 + r_A/x$$

Equation (14) is similar to the penultimate effect composition equation given above; it may also be illustrated by the plot in Fig. 2 from which we obtain

$$r_{BB} = 4 \frac{r_{2A}}{r_2} \frac{1+r}{1+r_{A42}} = 0.30 \quad \text{and} \quad r_{AB} = r_{A4A} \frac{1+r_{A42}}{r_{A42}} = 0.70$$

It is also possible to calculate the relative rate of 1,2- and 1,4-addition for the butadiene units $dB_2/dB_4 = b$. Using Eqs. (3), (4), (7), (8), and (9), the relations derived from the steady-state assumption, and from Eqs. (12) and (13), we obtain

$$b = \frac{1 + r_{2A}(1 + r_2)x/r_2}{1 + 3 \frac{r_{2A}}{r_2} (1 + r_2)x + r_{A42}(2 + 1/r_{A4A}x)} \quad (15)$$

It may be seen that the limiting value of b/x when x tends to be null is r_{A4A}/r_{A42} . From the slope of the linear relation between the 1,2-addition and the butadiene content, we obtain

$$r_{A4A}/r_{A42} = k_{A42}/k_{A4A} = 0.33$$

Thus we have $r_{A4A} = 0.37$ and $r_{A42} = 1.1$. In addition, we have

$$r_{2A} = 0.16 \frac{r_2}{1 + r_2} \quad \text{and} \quad r_{4A} = 0.105 \frac{3r_2 + 2}{1 + r_2}$$

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