COPOLYMERIZATION

Part 1.—Monomer Reactivity Ratios in the Copolymerization of Acrylonitrile with Vinyl Bromide and of Acrylonitrile with Allyl Alcohol

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(Received August 10, 1967)

A study of the free radical induced copolymerization of acrylonitrile (M_1) with vinyl bromide (M_2) and that of acrylonitrile (M_1) with allyl alcohol (M_2) has been made. The monomer reactivity ratios, r_1 and r_2, in both systems have been evaluated by using methods based on both the differential and the integrated forms of the copolymerization composition equation. The values of r_1 and r_2 found by different methods are in good agreement in both cases. By taking mean of all r_1 and r_2 values found by different methods, the results obtained are $r_1 = 2.8$ and $r_2 = 0.14$ for the monomer pair acrylonitrile–vinyl bromide and $r_1 = 1.87$ and $r_2 = 0.05$ for the monomer pair acrylonitrile–allyl alcohol. The theoretical curves obtained for both systems by using these values in the copolymerization composition equation are found to fit well to the experimental results.

The Q–e scheme of Alfrey and Price has been used to calculate the reactivity ratios for the acrylonitrile–vinyl bromide monomer pair. The calculated values ($r_1 = 2.73$ and $r_2 = 0.16$) are in excellent agreement with the observed values. The reactivity ratios for both the monomer pairs have also been calculated by using the theory recently proposed by Bamford, Jenkins and Johnston on the basis of the modified Hammett equation,

$$\log k = \log k_T + \alpha\sigma + \beta$$

The theoretical values obtained by this method for r_1 and r_2 in both cases are regarded to be in reasonable agreement with the observed values.

Introduction

In the kinetic analysis of a radical copolymerization it is usually assumed that the reactivity of a polymer radical is independent of its chain length and the reactivity is governed entirely by the terminal monomer unit. On this assumption, the copolymerization of a pair of monomers M_1 and M_2 involves two types of polymer radicals $M_1^\bullet$ and $M_2^\bullet$ and four distinct growth reactions:

$$M_1^\bullet + M_1 \xrightarrow{k_{11}} M_1^\bullet, \quad (\text{rate} = k_{11}\,[M_1^\bullet]\,[M_1]) \quad (1)$$

$$M_1^\bullet + M_2 \xrightarrow{k_{12}} M_2^\bullet, \quad (\text{rate} = k_{12}\,[M_1^\bullet]\,[M_2]) \quad (2)$$

$$M_2^\bullet + M_1 \xrightarrow{k_{21}} M_1^\bullet, \quad (\text{rate} = k_{21}\,[M_2^\bullet]\,[M_1]) \quad (3)$$

$$M_2^\bullet + M_2 \xrightarrow{k_{22}} M_2^\bullet, \quad (\text{rate} = k_{22}\,[M_2^\bullet]\,[M_2]) \quad (4)$$

Here, the subscript on the radical designates the unit last added to it. The first subscript attached to the rate constant, i.e., k_{11}, k_{12}, k_{21} or k_{22}, refers to the reacting radical and the second to the monomer. The bracketted term in a rate equation denotes the concentration of the species in moles/litre. The ratios k_{11}/k_{12} and k_{22}/k_{21} are defined as the monomer reactivity ratios, r_1 and r_2. In a binary copolymerization in the absence of a solvent, there are four transfer-to-monomer reactions as shown above, and mutual termination of the polymer radical chains can result from three types of radical interaction.

Assuming steady-state conditions where the rate of creation of any type of polymer radicals, i.e., $M_1^\bullet$ or $M_2^\bullet$ is equal to the rate of its destruction, one can obtain the copolymerization composition equation [1,2,3] as follows:

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1\,[M_1] + [M_2]}{r_2\,[M_2] + [M_1]} \quad (5)$$

where the quantity $d[M_1]/\,d[M_2]$ represents the ratio of the two monomers in the increment of copolymer formed and $[M_1]$ and $[M_2]$ are the concentrations of the two monomers in the reaction mixture. The reactivity ratios,[4] r_1 and r_2 in the copolymerization composition equation (5) are unaffected in most cases by the presence of inhibitors, chain transfer agents, solvents and a small quantity of impurities.

The polymers and copolymers of acrylonitrile are industrially very important. The consumption of acrylonitrile is very large in the rubber, plastic and fibre industries.[5] The copolymerizations of acrylonitrile with a large number of vinyl monomers together with the values of their reactivity ratios have already been reported in the literature,[6] while for some compounds such data are still lacking. The increasingly industrial importance of acrylonitrile demands the experi-

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mental determination of the reactivity ratios in the copolymerizations of this monomer with other vinyl monomers.

In this paper the reactivity ratios of benzoyl peroxide initiated copolymerizations of acrylonitrile with vinyl bromide and with allyl alcohol have been reported, and a comparative study of the different methods for the determination of reactivity ratios in a copolymerization system has been made with reference to the results presented here.

Experimental

Materials.—Acrylonitrile (B.D.H.) was dried over (Na_2SO_4) and distilled in an atmosphere of nitrogen. The middle fraction (b.p. 76.2°C) was collected and stored at 0°C in the dark.

Vinyl bromide was prepared by modifying the method of Regnault.[7] The modified method,[8] which gives high yield in a short time, consists of dropping 150 ml ethylene dibromide for about 5 hr into a mixture of 100 ml water, 100 ml ethyl alcohol and 150 g caustic potash beads maintained at a temperature of about 70°C. Vinyl bromide evolving as a gas was first passed through a calcium chloride column, then through a column packed with caustic potash beads at room temperature and ultimately cooled by a dry ice–acetone mixture. The yield of vinyl bromide was 100 to 105 ml at 0°C. The monomer (b.p. 16°C) was stored at 0°C in the absence of light.

Allyl alcohol (B.D.H.) was dried over (Na_2SO_4) and distilled. The middle third (b.p. 97°C) was used.

Benzoyl peroxide (B.D.H.) was recrystallized twice from chloroform by the addition of methanol. The recrystallized product was dried under vacuum at room temperature and stored at 0°C in the dark.

Procedure.—All the copolymerization reactions were performed in sealed Pyrex tubes. A weighed amount of the initiator (0.040 g) was first poured through a funnel ending in a capillary into a graduated Pyrex tube kept at 0°C. Then acrylonitrile was pipetted into the tube and this was followed by the addition of vinyl bromide to the desired mark of the tube. This procedure of charging the reaction tube had to be applied because of high volatility of vinyl bromide. The same procedure of charging the reaction tube was used for the copolymerization of acrylonitrile with allyl alcohol. Finally, the tube with its contents was sealed carefully, and heated in a thermostat bath.

After the desired time of heating, the seal was broken and the contents of the tube were taken in methanol. The precipitated copolymer was filtered and dried under vacuum at room temperature. The same operation could not be used for the copolymer of acrylonitrile with allyl alcohol because of its partial solubility in methanol. This copolymer was directly dried in the reaction tube under vacuum at room temperature.

The copolymer of acrylonitrile with vinyl bromide was mostly insoluble in tetrahydrofuran. The proportion of insoluble fraction formed was dependent upon the concentration of acrylonitrile monomer in feed. The bromine and nitrogen analysis for both the fractions indicated that the insoluble fraction contained more nitrogen and less bromine than the soluble fraction and *vice versa.* Experiments have shown that polyvinyl bromide prepared under similar conditions as described here is completely soluble in tetrahydrofuran, and similarly prepared polyacrylonitrile is completely insoluble in this solvent. This proves beyond doubt that the polymer formed by the reaction of acrylonitrile with vinyl bromide in the presence of benzoyl peroxide initiator is a copolymer.

The copolymer of acrylonitrile with allyl alcohol was mostly soluble in acetone, although polyacrylonitrile prepared under the same conditions in the absence of allyl alcohol was completely insoluble in this solvent. The nitrogen analysis of both the soluble and insoluble fractions of this copolymer in acetone indicated that the soluble fraction contained 2–3% less nitrogen than the insoluble fraction and *vice versa.* This analysis shows that the product obtained by the polymerization of acrylonitrile with allyl alcohol is a copolymer.

Analyses.[9]—The copolymer of acrylonitrile with vinyl bromide was analyzed for bromine by burning a small quantity (40 to 50 mg) of it on a filter paper in oxygen (Schoniger combustion). The resulting gaseous product was absorbed in 10 ml of 0.1N sodium hydroxide solution containing 5 drops of 40% hydrogen peroxide. Finally, this solution was titrated for bromine using the Volhard's method.[10] The accuracy of analysis by this method was checked by using the method of Carius. The deviation observed was within ±0.5%.

The copolymers of acrylonitrile with allyl alcohol and of acrylonitrile with vinyl bromide were analyzed for nitrogen using Kjeldahl method. The method was standardized by the analysis of

TABLE 1.—COPOLYMERIZATION OF ACRYLONITRILE $[M_1]$ WITH VINYL BROMIDE $[M_2]$ AT 60.0 ± 0.1°C USING 0.8% (w/w) BENZOYL PEROXIDE AS INITIATOR, THE DURATION OF THE REACTION BEING 3.50 HR IN EVERY CASE.

Acrylonitrile in feed, $[M_1]_0$ mmoles	Vinyl bromide in feed, $[M_2]_0$ mmoles	Acrylonitrile unreacted, $[M_1]$ mmoles	Vinyl bromide unreacted, $[M_2]$ mmoles	% Nitrogen in copolymer	% Bromine in copolymer
0.0	46.73	0.0	40.00	0.0	73.20
18.80	36.90	15.50	36.10	17.80	24.20
37.70	28.40	28.30	26.50	18.90	21.30
46.80	22.70	30.60	20.10	19.30	18.00
56.60	15.60	23.80	11.10	22.09	13.70
75.50	9.20	31.60	7.00	23.50	6.90
84.80	4.50	11.10	2.90	25.40	3.10

TABLE 2.—COPOLYMERIZATION OF ACRYLONITRILE $[M_1]$ WITH ALLYL ALCOHOL $[M_2]$ AT 50.0 ± 0.1°C USING 0.8% (w/w) BENZOYL PEROXIDE AS INITIATOR, THE DURATION OF THE REACTION BEING 15.00 HR IN EVERY CASE.

Acrylonitrile in feed, $[M_1]_0$ mmoles	Allyl alcohol in feed, $[M_2]_0$ mmoles	Acrylonitrile unreated, $[M_1]$ mmoles	Allyl alcohol unreacted, $[M_2]$ mmoles	% Nitrogen in copolymer
18.70	68.70	16.10	67.00	15.40
28.20	60.30	25.90	59.00	16.30
37.60	51.50	32.00	49.10	17.80
46.90	43.00	40.10	40.40	18.90
56.60	34.40	54.90	34.00	22.20

pure polyacrylonitrile and of urea. The accuracy of this analysis was within ± 1%.

Results and Discussion

The detailed results of the copolymerization of acrylonitrile with vinyl bromide are given in Table 1, and those of acrylonitrile with allyl alcohol are shown in Table 2.

In the intersection method of Mayo and Lewis,[2] Equation (5) is integrated and a relation of the following type is obtained:

$$r_2 = \frac{\ln\dfrac{[M_2]_0}{[M_2]} - \left\{\dfrac{1}{p}\ln\dfrac{1-p\,([M_1]/[M_2])}{1-p\,([M_1]_0/[M_2]_0)}\right\}}{\ln\dfrac{[M_1]_0}{[M_1]} - \left\{\ln\dfrac{1-p\,([M_1]/[M_2])}{1-p\,([M_1]_0/[M_2]_0)}\right\}} \qquad (6)$$

where $[M_1]_0$ and $[M_2]_0$ are the monomer concentrations in feed, $[M_1]$ and $[M_2]$ are the monomer concentrations when the reaction is stopped, and $p=(1-r_1)/(1-r_2)$. Arbitrary values for p are chosen to find the corresponding values for r_1 and r_2 in a significant region. Thus a plot of r_1 values against r_2 values will give a straight line for each copolymerization reaction. Only two copolymerization reactions performed under exactly the same experimental conditions but with different monomer compositions in feed will fulfil the requirements for Mayo and Lewis method. The point of intersection of the two lines will give r_1 and r_2. Generally, three or more copolymerization reactions are performed to find the range of experimental error involved in the determination of r_1 and r_2 values.

Using equation (6) we have plotted our results of the copolymerization of acrylonitrile with vinyl bromide in Fig. 1, and of acrylonitrile with allyl alcohol in Fig. 1a. In either case the reactivity ratio r_1 of the common monomer acrylonitrile is taken as the ordinate and that of vinyl bromide or allyl alcohol, r_2 as the abscissa. In each case the straight lines obtained have intersected more or less at one point. This indicates, as Mayo and

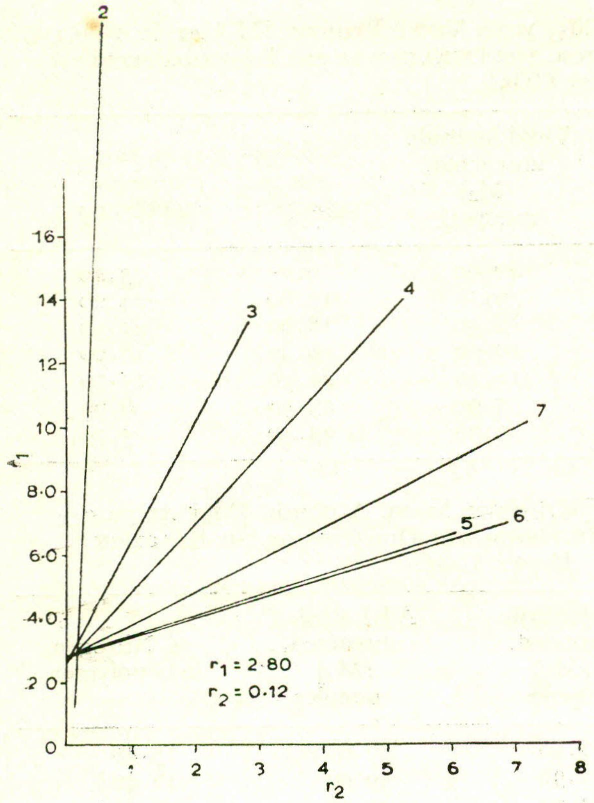

Fig. 1.—A plot of r_1 against r_2 for the copolymerization of acrylonitrile (M_1) with vinyl bromide (M_2) according to the method of Mayo and Lewis.[2] The numbering of the straight lines correspond to the order of experiments in Table 1.

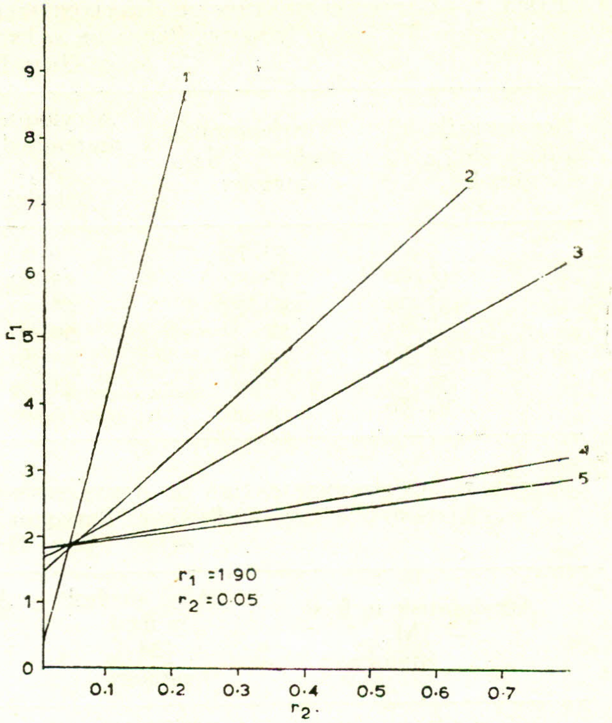

Fig. 1a.—A plot of r_1 versus r_2 for the copolymerization of acrylonitrile (M_1) with allyl alcohol (M_2) according to the method of Mayo and Lewis.[2] The numbering of the straight lines correspond to the order of experiments in Table 2.

Lewis[2] have pointed out in such a case, that the uncertainty involved in the isolation, purification and chemical analysis of the individual copolymer is minimum. The reactivity ratios obtained by Mayo plot for the monomer pair acrylonitrile—vinyl bromide are $r_1 = 2.8 \pm 0.1$ and $r_2 = 0.12 \pm 0.05$, and for the monomer pair acrylonitrile—allyl alcohol are $r_1 = 1.9 \pm 0.1$ and $r_2 = 0.050 \pm 0.005$.

In the case of Fineman and Ross' method,[11] the copolymer ratio, $d[M_1]/d[M_2]$ in equation (5) is replaced by f and the monomer ratio, $(M_1)/(M_2)$ by F to obtain the following equation:

$$F(f-1)/f = r_1 F^2/f - r_2 \qquad (7)$$

The slope and the intercept of the plot of $F(f-1)/f$ versus F^2/f are r_1 and $-r_2$, respectively. This type of plot with our results is shown in Fig. 2 for the monomer pair acrylonitrile–vinyl bromide and in Fig. 2a for the monomer pair acrylonitrile–allyl alcohol. In the former case, the reactivity ratios obtained are $r_1 = 2.70$ and $r_2 = 0.15$, and in the latter case, $r_1 = 1.87$ and $r_2 = 0.04$. These results are in good agreement with those obtained by the use of equation (6).

The modified form of Fineman and Ross' equation,[12] which is the same as equation (5) expressed in mole fractions of monomer M_1, is given by

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = r_2 + \frac{f_1{}^2(F_1-1)}{(1-f_1)2F_1} r_1 \qquad (8)$$

where f_1 $[=1-f_2=[M_1]/([M_1]+[M_2])]$ denotes the mole fraction of monomer M_1 in feed, F_1 $[=1-F_2=d[M_1]/d([M_1]+[M_2])]$ represents the mole fraction of M_1 units in the increment of copolymer formed at the initial stage of copolymerization, and f_2 and F_2 are the corresponding terms for the conjugate monomer M_2. The plots of $f_1(1-2F_1)/(1-f_1)F_1$ versus $f^2{}_1\,(F_1-1)/(1-f_1)2F_1$ with the data in Tables 1 and 2 give the curves shown in Fig. 3 and Fig. 3a, respectively. The reactivity ratios obtained by these plots are $r_1 = 2.90$ and $r_2 = 0.15$ for acrylonitrile–vinyl bromide monomer pair (Fig. 3) and $r_1 = 1.83$ and $r_2 = 0.05$ for acrylonitrile—allyl alcohol monomer pair

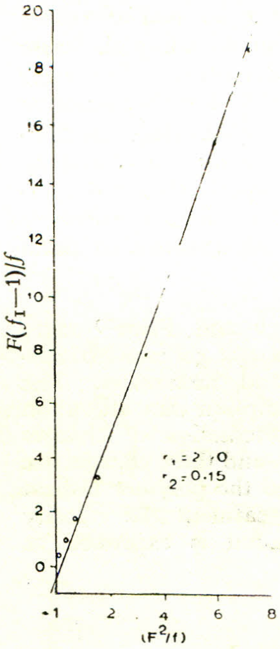

Fig. 2.—$F(f-1)/f$ is plotted against F^2/f using the mole ratio method of Fineman and Ross[11] for the copolymerization of acrylonitrile (M_1) with vinyl bromide (M_2).

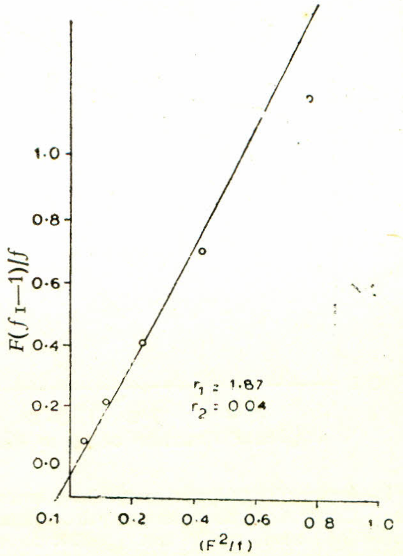

Fig. 2a.—$F(f-1)/f$ is plotted against F^2/f using the mole ratio method of Fineman and Ross[11] for the copolymerization of acrylonitrile (M_1) with allyl alcohol (M_2).

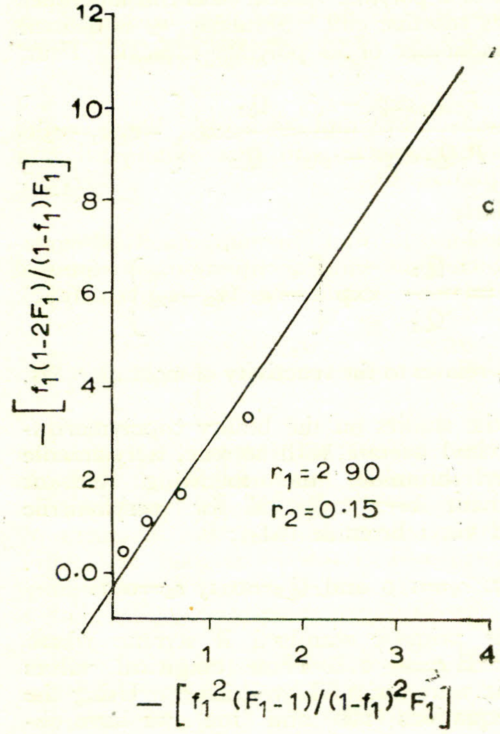

Fig. 3.—A plot of $f_1(1-2F_1)/(1-f_1)F_1$ against $f_1{}^2-[(F_1-1)/(1-f_1)2F_1]$ according to the mole fraction method of Fineman and Ross[12] for the copolymerization of acrylonitrile (M_1) with vinyl bromide (M_2).

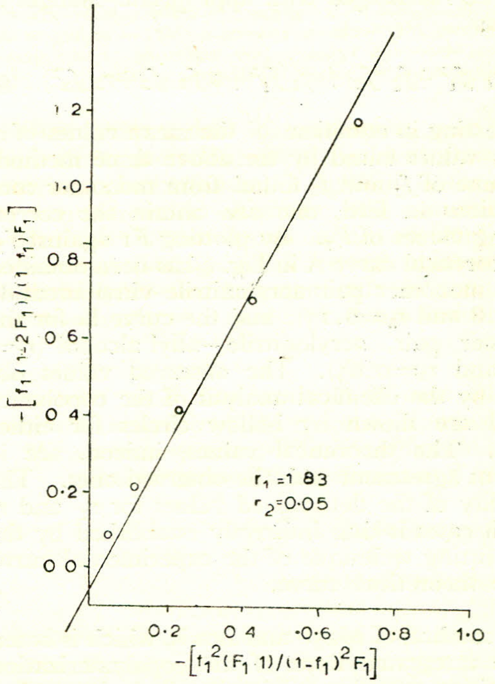

Fig. 3a.—A plot of $f_1(1-2F_1)/(1-f_1)F_1$ against $[f_1{}^2(F_1-1)/(1-f_1)2F_1]$ according to the mole fraction method of Fineman and Ross[12] for the copolymerization of acrylonitrile (M_1) with allyl alcohol (M_2).

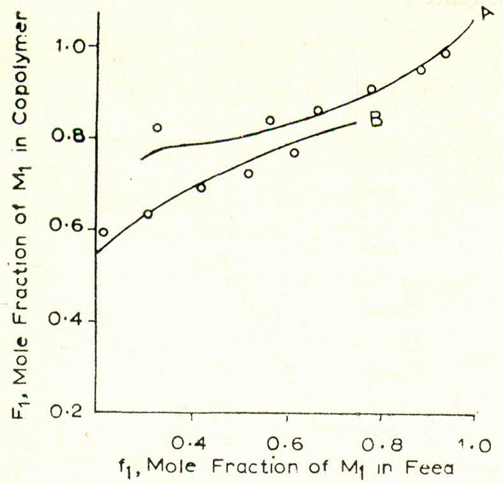

Fig. 4.—A plot of copolymer composition versus monomer composition. Curve A for the monomer pair acrylonitrile(M_1)—vinyl bromide (M_2) where $r_1=2.8$ and $r_2=0.14$; curve B for the monomer pair acrylonitrile(M_1)—allyl alcohol (M_2) where $r_1=1.87$ and $r_2=0.05$. The experimental results are shown by hollow circles in each case.

(Fig. 3a). These reactivity ratios are more or less the same as those obtained by using equations (6) and (7).

The copolymerization composition equation (8) could be rearranged with appropriate changes as follows:

$$F_1=(r_1 f_1^2+f_1 f_2) / (r_1 f_1^2+2 f_1 f_2+r_2 f_2^2) \quad (9)$$

By inserting in equation (9) the mean values of r_1 and r_2 values found by the above three methods and those of f_1 and f_2 found from monomer concentrations in feed, one can obtain the corresponding values of F_1. By plotting F_1 against f_1, the theoretical curve A in Fig. 4 has been obtained for the monomer pair acrylonitrile–vinyl bromide ($r_1=2.8$ and $r_2=0.15$), and the curve B, for the monomer pair, acrylonitrile—allyl alcohol ($r_1=1.87$ and $r_2=0.05$). The observed values obtained by the chemical analysis of the copolymer formed are shown by hollow circles for either system. The theoretical values, indeed, are in excellent agreement with the observed ones. The reliability of the determined values for r_1 and r_2 in both cases is thus indirectly established by the above fitting technique of the experimental curve on the theoretical curve.

The method of Mayo and Lewis, which is based on the integrated form of the copolymerization composition equation (5) is versatile in its use but involves complicated calculations. Both the methods of Fineman and Ross, which are based on the differential form of the copolymerization composition equation can only be used at a very low conversion of copolymers, although these involve less complicated calculations. The mole ratio method of Fineman and Ross is very sensitive to small experimental error. As a result it is difficult to assess the accurate values for r_1 and r_2, unless a large number of experiments are performed. The mole fraction method is preferabe in this respect, since it is less sensitive to small experimental error.

The *Q-e* scheme of Alfrey and Price[13] takes account of both polar effects and general reactivities of polymer radicals and monomers. The scheme is based on the assumption that alteration results from electrostatic interaction of charges on the radical and monomer, and these charges are the same for a monomer and the polymer radical derived from it. In this treatment the velocity constant for cross propagation is expressed as follows:

$$k_{12}=P_1Q_2\exp(-e_1e_2) \quad (10a)$$

where P_1 and Q_2 refer to the reactivities of the polymer radical $M_1^\bullet$ and the monomer M_2, respectively, and e_1 is a measure of the charge on M_1 monomer or a polymer radical with this monomer unit at its reactive end. Similarly, e_2 is defined for M_2 monomer or its polymer radical. Thus,

$$r_1=\frac{k_{11}}{k_{12}}=\frac{P_1Q_1\exp(-e_1^2)}{P_1Q_2\exp(-e_1e_2)}=\frac{Q_1}{Q_2}\exp\left[-e_1(e_1-e_2)\right] \quad (10b)$$

and similarly

$$r_2=\frac{k_{22}}{k_{21}}=\frac{Q_2}{Q_1}\exp\left[-e_2(e_2-e_1)\right] \quad (10c)$$

where Q_1 relates to the reactivity of monomer M_1.

From the studies on the binary copolymerizations of vinyl acetate with styrene, acrylonitrile and vinyl bromide, the following relevant data[14,15] have been collected for acrylonitrile (M_1) and vinyl bromide (M_2):

$Q_1=0.67$, $e_1=1.0$ and $Q_2=0.1$, $e_2=0.1$.

where the primary standard is styrene whose $Q=1.0$ and $e=-0.8$. These empirical values for styrene were assigned by Price.[16] Using the data in equations (10b) and (10c), we have obtained the values for the reactivity ratios for the monomer pair acrylonitrile—vinyl bromide as $r_1=2.73$ and $r_2=0.16$. These are in excellent agreement with the r_1 and r_2 values obtained by other methods. However, similar data for allyl alcohol are not available in the literature.

The recently developed theory of Bamford, Jekins and Jonhston[17] for assessing the extent of contribution of polar effects in the transition state to chain transfer and copolymerization reactions has been utilized to calculate the monomer reactivity ratios in both the copolymerization systems under study. In this theory the reactivity of a polymer radical in the radical displacement reaction with toluene (velocity constant, k_T) is chosen as the general standard. The polar effects in this reaction are likely to be of little importance since toluene is more or less electronically neutral. The velocity constant, k for the reaction of the polymer radical with any other substrate, whether a monomer or a transfer agent, can be expressed as follows:

$$\log k = \log k_T + \alpha\sigma + \beta \qquad (11a)$$

where σ is the algebraic sum of Hammett sigma constants for the substituents in the terminal monomer unit of the radical; α a polar constant for the monomer and β a resonance constant for the monomer. Further, α is related to σ by the relation, $\alpha = -5.3\,\sigma$. In this treatment, β is a measure of the general reactivity of the monomer and the term $\alpha\sigma$ indicates the extent to which polar effects contribute to the velocity constant for a reaction involving the polymer radical. However, the magnitude of this term will depend upon properties of both the polymer radical and the substrate.

Applying equation (11a) to the competition between growth reactions in a copolymerization, reactions (1)-(4), one can obtain

$$\log r_1 = \log (k_{11}/k_{12}) = (\alpha_1 - \alpha_2)\ \sigma_1 + (\beta_1 - \beta_2) \qquad (11b)$$

and $$\log r_2 = \log (k_{22}/k_{21}) = (\alpha_2 - \alpha_1)\sigma_2 + (\beta_2 - \beta_1) \qquad (11c)$$

where α_1 and β_1 refer to M_1, α_2 and β_2 to M_2, and σ_1 refers to polymer radical $M_1\cdot$ and σ_2 to polymer radical $M_2\cdot$. However, it is interesting to note here that if equations (11b) and (11c) are rearranged in the exponential form, these will be similar to equations (10b) and (10c), respectively, derived from the $Q-e$ treatment.

The relevant data for all the three monomers have been collected in Table 3 from the data compiled by Bamford and Jenkins[18] for a large number of monomers. Using these data in equations (11b) and (11c), we have calculated the reactivity ratios for both the monomer pairs. The values obtained for the monomer pair acrylonitrile (M_1)-vinyl bromide (M_2) are $r_1 = 3.09$ and $r_2 = 0.06$, and for the monomer pair acrylonitrile (M_1)–allyl alcohol (M_2) are $r_1 = 3.51$ and $r_2 = 0.10$. These values of r_1 and r_2 in both systems (except r_2 for vinyl bromide) are much higher than those obtained by other methods (Table 5). Higher values for r_1 and r_2 are also found for many other monomer pairs. Using the theory of Bamford *et al.*,[17] we have calculated the reactivity ratios for a number of monomer pairs and compared the calculated values with those obtained experimentally by other workers (Table 4).

TABLE 3.—α AND β VALUES FOR MONOMERS, AND σ VALUES FOR THE CORRESPONDING POLYMER RADICALS.

Monomer	α	β	σ
Acrylonitrile	−3.0	5.3	0.57
Vinyl bromide	−1.0	3.67	0.19
Allyl alcohol	−1.5	3.9	0.28

TABLE 4.—A COMPARISON OF THE OBSERVED AND THE CALCULATED REACTIVITY RATIOS IN THE BINARY COPOLYMERIZATIONS OF ACRYLONITRILE (M_1) WITH SOME VINYL MONOMERS (M_2).

Copolymerization of acrylonitrile with	Observed values (Mayo and Lewis)[2]		Calculated values (Bamford *et al.*)[17]	
	r_1	r_2	r_1	r_2
Vinyl benzoate[19]	5.0	0.05	8.32	0.021
Vinyl chloride[20]	3.28	0.02	6.24	0.059
Vinyl chloride[21]	3.7	0.074		
Allyl chloride[19]	3.0	0.05	5.50	0.032
Tetrachloroethylene[22]	470	0	446.70	0.002
Trichloroethylene[23]	67	0	73.28	0.012

The discrepancy between the observed and the calculated values of r_1 and r_2 is quite large in most of the cases (Table 4). The cause of such a discrepancy is not understood. This may be due to the error involved in the indirect evaluation of the monomer reactivity parameters (α, β and σ) from the parameters of the conjugate monomer in a binary copolymerization.

The values of the reactivity ratios obtained by different methods for the monomer pairs acrylonitrile–vinyl bromide and acrylonitrile–allyl alcohol are given in Table 5. It is evident from

Table 5.—A Comparative Study of the Values of Reactivity Ratios Obtained by Different Methods in the Copolymerization of Acrylonitrile [M_1] with Vinyl Bromide [M_2] and of Acrylonitrile [M_1] with Allyl Alcohol [M_2].

Method	Acrylonitrile—vinyl bromide copolymerization		Acrylonitrile—allyl alcohol copolymerization	
	r_1	r_2	r_1	r_2
Mayo and Lewis[2]	2.8 ± 0.1	0.12 ± 0.05	1.9 ± 0.1	0.050 ± 0.005
Fineman and Ross[11] (mole ratio equation)	2.70	0.15	1.87	0.04
Fineman and Ross[12] (mole fraction equation)	2.90	0.15	1.83	0.05
Alfrey and Price[13] (Q—e scheme)	2.73	0.16	—	—
Bamford *et al.*[17] (modified Hammett equation)	3.09	0.06	3.51	0.10

the table that the values of r_1 and r_2 evaluated by the methods based on the integrated and the differential forms of the copolymerization composition equation are in good agreement for both the systems.

The *Q—e* scheme[13] has proved successful for the monomer pair acrylonitrile–vinyl bromide. Similar is the case with many other monomer pairs, although the scheme is not theoretically sound.[24] The theory of Bamford *et al.*[13] covers the reactions of a wide range of monomers but the values obtained for the reactivity ratios of monomers by its use differ in many cases from the experimentally determined values even by a factor of two (Table 4). Considering this, the values of the monomer reactivity ratios obtained for both systems by this method are considered to be very satisfactory.

Both the copolymerization systems are non-azeotropic[25] since one reactivity ratio is greater than unity and the other is less than unity. Furthermore, since both r_1 and $1/r_2$ are greater than unity, both radicals in either system prefer the same monomer. In other words, acrylonitrile monomer in both systems is more reactive than the other with respect to either radical. This is more prominent in the acrylonitrile—allyl alcohol system where acrylonitrile is about two times as reactive as allyl alcohol towards the polyacrylonitrile radical but polyallyl alcohol radical prefers to adding acrylonitrile monomer by a factor of about twenty as compared with the addition of allyl alcohol monomer. Hence polymerization of a mixture of similar amounts of acrylonitrile and allyl alcohol yields an initial product which is almost pure polyacrylonitrile. Only after most of acrylonitrile has polymerized is a copolymer formed which contains a comparable proportion of allyl alcohol.

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