COPOLYMERIZATION OF ACRYLONITRILE AND ALLYL ACETATE AND DETERMINATION OF THEIR REACTIVITY RATIOS

S.A.K. Lodhi and A. Rasheed Khan

Physical Research Division, P.C.S.I.R. Laboratories, Karachi 39

Copolymerization of acrylonitrile and allyl acetate with benzoyl peroxide as catalyst was carried out at $75 \pm 0.1°C$. Monomer reactivity ratios were determined experimentaly using Mayo and Lewis, mole ratio and mole fraction methods. The values of r_A and r_B measured as above were then compared with the value obtained by the modified Hammett equation. The results show that acrylonitrile enters in copolymerization fifty times more rapidly than allyl acetate. Some of the physical properties of the copolymer formed are also studied.

The behaviour of two monomers M_A and M_B in free radical type of copolymerization may be described by the following relation,

$$\frac{d[M_A]}{d[M_B]} = \frac{[M_A]}{[M_B]} \times \frac{r_A[M_A] + [M_B]}{r_B[M_B] + [M_A]} \quad (1)$$

where $[M_A]$ and $[M_B]$ represent the concentration of the unreacted monomers in the reaction mixture, $d[M_A]/d[M_B]$ refers to the ratio of the two monomers in the increment of copolymer formed, r_A and r_B are reactivity ratios of the monomers. This equation is useful in measuring the factors which govern copolymerization reactions. In the differential form it is valid at any conversion for relating the instantaneously forming copolymers with instantaneous monomer compositions. On integrating equation 1, Mayo and Lewis[1] obtained the following expression,

$$r_B = \frac{\ln\frac{[M_B]_o}{[M_B]} - \left\{ \frac{1}{p}\ln\frac{1-p([M_A]/[M_B])}{1-p[M_A]_o/[M_B]_o} \right\}}{\ln\frac{[M_A]_o}{[M_A]} + \left\{ \ln\frac{1-p([M_A]/[M_B])}{1-p([M_A]_o/[M_B]_o} \right\}} \quad (2)$$

where $[M_A]_o$ and $[M_B]_o$ are the monomer concentration in feed, $p = (1-r_A)/(1-r_B)$. Positive or negative values of p are arbitrary chosen by trial and error to find the corresponding values of r_A and r_B. For any copolymerization reaction a plot of r_A versus r_B determined as above should give practically a straight line. Another reaction performed under identical conditions with different monomer feed will give a straight line plot of r_A-r_B. At the point of intersection the corresponding values of r_A and r_B read from the graph should give fairly an accurate estimate of the reactivity ratios. Usually more than three experiments with different $[M_A]_o$ and $[M_B]_o$ are performed to estimate the magnitude of error involved in values of r_A and r_B determined by the intersection method.

Using equation[1] Fineman and Ross[2] derived the following rate equation to determine r_A and r_B,

$$\frac{F}{f}(f-1) = r_A \frac{F^2}{f} - r_B \quad (3)$$

where f is $d[M_A]/d[M_B]$, F is monomer ratio, $[M_A]/(M_B)$. A plot of $F(f-1)/f$ against F^2/f is a straight line whose slope is r_A and intercept r_B. This is called mole ratio equation.

The modified form of Fineman and Ross equation expressed in mole fractions of monomer is written as,[3]

$$\frac{f_A(1-2F_A)}{(1-f_A)F_A} = r_B + \frac{f^2_A(F_A-1)}{(1-f_A)^2F_A}r_A \quad (4)$$

where f_A represents the mole fraction of monomer in feed, F_A the mole fraction of monomer in the increment of copolymer formed at the start of copolymerization.

The copolymerization of acrylonitrile with different monomers has already been studied by many workers. This paper describes the copolymerization of acrylonitrile and allyl acetate using benzoly peroxide as initiator with a view to determine monomer reactivity ratios. To arrive at a better estimate of the reactivity ratio values comparative study of different methods is undertaken. Some of the physical properties of the copolymer formed are also reported.

Experimental

Procedure.—All copolymerization reactions were carried out in sealed Pyrex-glass tubes, 30 cm long and 20 cm internal diameter. 1.25 g acrylonitrile and 1.25 g allyl acetate were transfered through a long stem funnel into the reaction tube kept at 0°C. To this 0.025 g benzoyl peroxide was added and the tube sealed at the constriction. The reaction tube was then placed in a thermostatic bath whose temperature was maintained at $75 \pm 0.1°C$. Several trial runs were carried, which indicated that after about 3 hr the entire amount of acrylonitrile polymerized.

Proceeding in the manner mentioned above four sets of experiments were performed taking different proportions of monomers in feed, as described in Table 1, with 1% (w/w) of the catalyst. The reaction was allowed to proceed for 1 hr after which the seal was broken open, copolymer formed was transferred to the cintered glass funnel and washed several times with methanol, then dried under reduced pressure to a constant weight.

The nitrogen contents of the copolymer formed in each tube were determined using Kjeldahl's method. The estimations were standardized by the nitrogen analysis of polyacrylonitrile and phenyl thiourea. The accuracy of our determinations was 0.8%.

Viscosity of the copolymer solutions was measured by using Ostwald's type viscometer (Technico 1, B.S. No. 188). The time of flow was measured by a stopwatch graduated up to 1/10th of a second. The stopwatch was calibrated with a wrist watch having an accuracy of 20 sec in 24 hr. The accuracy of observations was tested by measuring the viscosity of pure water and N,N'-dimethylformamide, respectively at 25°C. The deviation from the standard values was ±0.005 cP. The temperature control which is extremely necessary in viscosity measurement was achieved by keeping the viscometer in a thermostatic bath (Townson and Mercer Ltd. S. No. 11262). The temperature fluctuations in the thermostatic bath was ±0.05°C.

Materials

Acrylonitrile of British Drug House was distilled. The fraction boiling at 76.2°C/760 mm Hg was collected and stored in a dark container after drying over sodium sulphate.

Preparation of Allyl Acetate.—Pure allyl alcohol (100g) acetic anhydride (200 g) with a little of concentrated sulphuric acid was refluxed for 2 hr The mixture was then allowed to cool and poured over cold water. The ester floats above the surface of water from where it is separated and washed with dilute sodium carbonate, then dried over calcium chloride. B.p. 103–104°C.

Benzoyl peroxide of the reagent grade was purified twice by dissolving in chloroform and precipitating by the addition of methanol. It was then dried under reduced pressure.

Laboratory grade methanol and N,N'-dimethyl formamide were purified by distillation.

Results and Discussion

The data collected from the studies of the system, acrylonitrile and allyl acetate are summarized in Table 2. Our analysis gave 25.6% nitrogen in the prepared sample of polyacrylonitrile. The resulting product of all our four samples of the binary mixtures gave 4–20% less nitrogen than the calculated amount. This difference is due to the attachment of allyl acetate in the polymer chain of polyacrylonitrile and is sufficient proof that the product obtained by the reaction of acrylonitrile with allyl acetate in the presence of benzoyl peroxide is a copolymer.

Reactivity Ratios Determinations.—The reactivity ratios r_A and r_B were determined first by using

TABLE 1.—SHOWING THE AMOUNT OF ACRYLONITRILE AND ALLYL ACETATE IN DIFFERENT FEEDS.

Experiment No.	Acrylonitrile in g	Allyl acetate in g	Total weight in g
1	1.00	1.50	2.50
2	1.25	1.25	2.50
3	1.75	0.75	2.50
4	2.00	0.50	2.50

TABLE 2.—COLLECTED DATA FROM THE STUDIES OF SYSTEM ACRYLONITRILE AND ALLYL ACETATE CARRIED OUT AT 75±0.1°C FOR 1 HR.

Experiment No.	Monomer in feed		Unreacted monomer		% nitrogen in the final product
	Acrylonitrile $[M_A]_0$ moles/l	Allyl acetate $[M_B]_0$ moles/l	Acrylonitrile $[M_A]$ moles/l	Allyl acetate $[M_B]$ moles/l	
1	6.575	5.226	3.461	4.567	18.9±0.8
2	8.104	4.295	3.939	3.659	20.5±0.8
3	11.040	2.508	4.612	2.043	23.3±0.8
4	12.410	1.644	4.818	1.312	24.4±0.8

intersection method. The r_A–r_B plot is shown in Fig. 1. The values obtained from this plot are, $r_A = 4.04 \pm 0.04$ and $r_B = 0.068 \pm 0.008$. The Fineman and Ross plot is shown in Fig. 2. The r_A and r_B values obtained from this plot are 2.85 ± 0.05 and 0.05 ± 0.02, respectively. According to equation 4 the plot of $f_A (1-2F_A)/(1-f_A) F_A$ against $f^2_A (F_A-1)/(1-f_A)^2 F_A$ is shown in Fig. 3. This gives the values of $r_A = 2.85 \pm 0.05$ and $r_B = 0.05 \pm 0.02$.

The monomer reactivity ratios given in Table 3 show that r_A and r_B values obtained by equation 3 and 4 are almost same but different from the one determined by equation 2. This is due to inherent inexactness of the experimental procedure. Better estimate of r_A and r_B could be made by using the following equation obtained by rearranging the copolymerization composition equation 4 with appropriate changes.

$$F_A = (r_A f_A^2 + f_A f_B)/(r_A f_A^2 + 2 f_A f_B + r_B f_B^2) \quad (5)$$

In this equation r_A and r_B are the mean of the values obtained by equations 2, 3 and 4, f_A and f_B are found from monomer concentration in feed. The points shown by hollow circles in Fig. 4 are obtained by plotting F_A determined by equation 5 against corresponding f_A. Similarly a plot of F_A using the relation,

$$F_A = \frac{d[M_A]}{d[M_A] + d[M_B]}$$

determined by the chemical analysis of the copolymer formed against f_A are shown by triangles. The calculated values plots are in good agreement with the observed values plots. The reliability
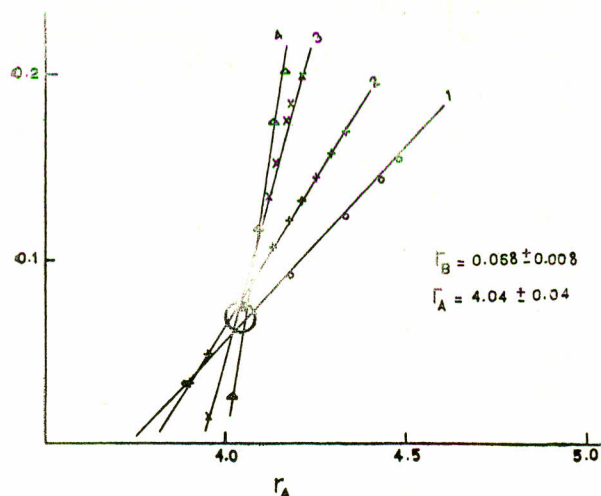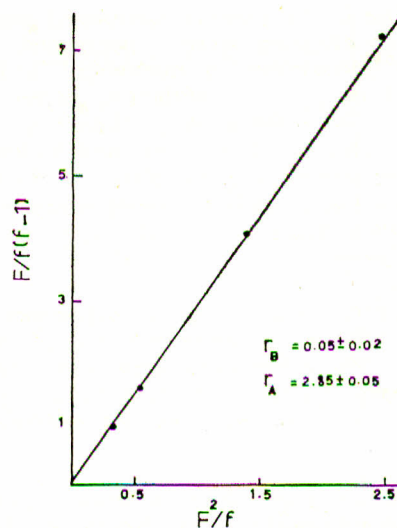

Fig. 2.—A plot of $F/f\,(f\text{-}1)$ versus F^2/f according to the mole ratio method to obtain r_A and r_B.
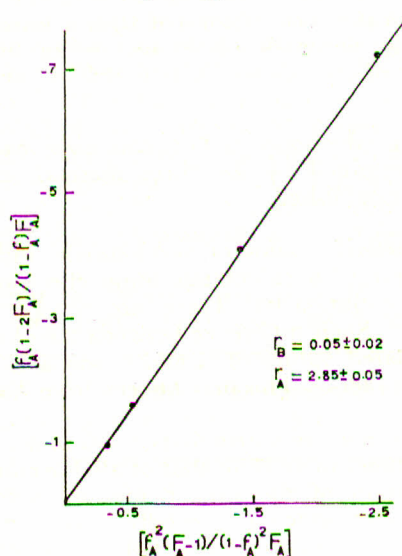
Fig. 3.—A plot of $f_A\,(1\text{-}2F_A)/(1\text{-}f_A)F_A$ against $f^2_A\,(F_A\text{-}1)/(1\text{-}f_A)^2 F_A$ to determine r_A and r_B values.

Fig. 1.—Mayo and Lewis plot of r_B against r_A for copolymerization of acrylonitrile and allyl acetate.

TABLE 3.—REACTIVITY RATIO VALUES r_A AND r_B DETERMINED BY DIFFERENT METHODS FOR ACRYLONITRILE AND ALLYL ACETATE COPOLYMERIZATION.

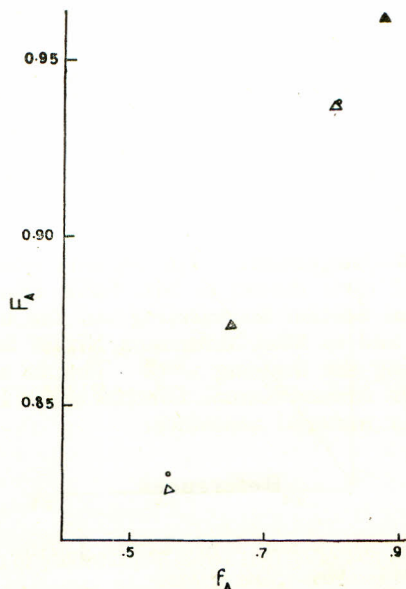| Method used	r_A	r_B
Mayo, and Lewis method	4.04 ± 0.04	0.068 ± 0.008
Mole ratio method	2.85 ± 0.05	0.05 ± 0.02
Mole fraction method	2.85 ± 0.05	0.05 ± 0.02
Modified Hammett equation	4.17	0.021

Fig. 4.—A plot of mole fraction of M_A in copolymer (F_A) against mole fraction of M_A in feed (f_A). Calculated values are shown by hallow circles and observed values are shown by triangles.

Fig. 5.—Plot showing the rate of polymerization of acrylonitrile in the presence of allyl acetate.

of r_A and r_B values obtained on averaging reactivity ratios determined by the three methods is thus indirectly established.

The reactivity ratios of acrylonitrile and allyl acetate were also calculated using the modified Hammett equation.[4,5] These are $r_A = 4.17$ and $r_B = 0.021$. Such difference between the observed and calculated values of r_A and r_B was also noted by other workers. This may be seen from Table 4.

Since the monomer reactivity ratio of acrylonitrile is 50 times more than that of allyl acetate the polymerization of the binary mixture gives an initial product which is virtually pure polyacrylonitrile. This is also supported by the plot of R_p against [AN] (Fig. 5), showing that, even in the presence of allyl acetate, rate of polymerization of acrylonitrile increases with increase in acrylonitrile concentration alone, in the initial stages. The plot of nitrogen percentage in the copolymer against mole ratio of AN to AA shown in Fig. 6 provides a further evidence that acrylonitrile enters in the copolymerization more rapidly than allyl acetate.

Molecular Weight of the Copolymer.—The number average molecular weight, $\overline{Mn}$ was determined by using the following relationship.[8]

$$[\eta] = 3.92 \times 10^{-4} \; \overline{Mn}^{\,0.75}$$

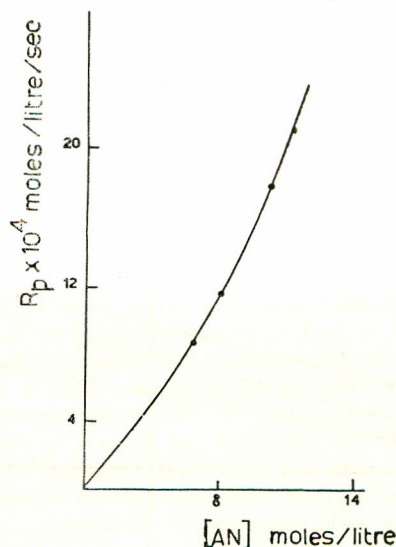where $[\eta]$ is the intrinsic viscosity of the copolymer solution. This is obtained by plotting η_{sp}/C
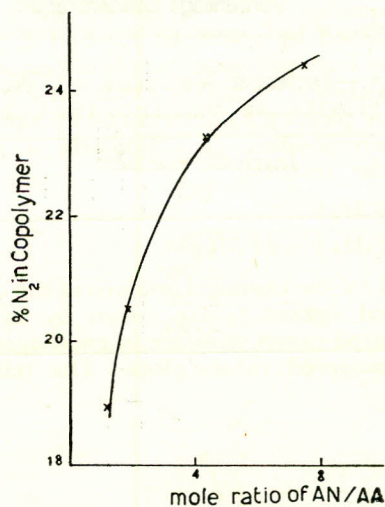

Fig. 6.—Graph showing the % of nitrogen in copolymer at different mole ratios of AN/AA.

TABLE 4.—A COMPARATIVE STUDY OF THE OBSERVED AND CALCULATED r_A AND r_B VALUES OBTAINED FROM THE COPOLYMERIZATION OF ACRYLONITRILE WITH VARIOUS MONOMERS.

Work reference	Copolymerization of acrylonitrile with	Observed		Calculated 5	
		r_A	r_B	r_A	r_B
Chapin et al.6	Vinyl benzoate	5.0	0.05	8.32	0.021
Chapin et al.6	Allyl chloride	3.0	0.05	5.50	0.032
Lewis et al.7	Vinyl chloride	3.28	0.02	6.24	0.059
This work	Allyl acetate	3.25	0.06	4.17	0.021

against C where η_{sp} is specific viscosity and C is the concentration of the solution expressed in percentage (Fig. 7). The average number molecular weight comes in the range 79,250 to 111,900. The detailed results are given in Table 5.
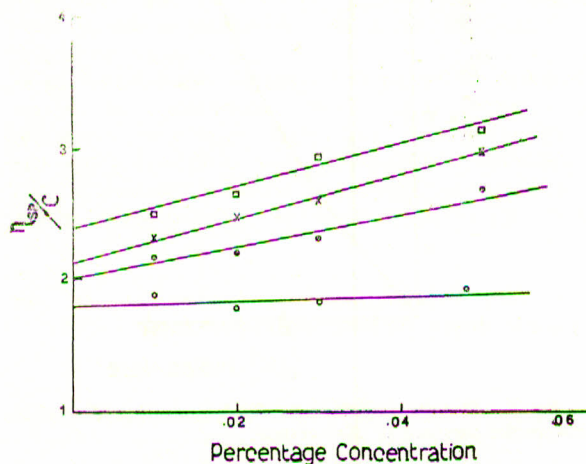

Fig. 7.—Plots of η_{sp}/C against percentage concentrations.

TABLE 5.—INTRINSIC VISCOSITY AND NUMBER AVERAGE MOLECULAR WEIGHT OF THE COPOLYMER.

Sample No	Intrinsic viscosity [η]	$\overline{M_n}$
1	1.80	79,250
2	2.00	87,700
3	2.12	94,620
4	2.40	111,900

Properties of the Copolymer.—The copolymer is white powdery substance and soluble in N, N'-dimethylformamide on warming. The solid begins to decompose at 208°C turning black at 270°C when it gets insoluble in N, N'-dimethylformamide. Polyacrylonitrile decomposes around 165° to 170°C gives mostly ionsoluble light black products.

References

1. F.R. Mayo and F.M. Lewis, J. Am. Chem. Soc., **66,** 1594 (1944).
2. M. Fineman and S.D. Ross, J. Polym. Sci., **5,** 259 (1950).
3. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, New York, 1953), p. 186.
4. C.H. Bamford, A.D. Jenkins and R. Johnston, Trans. Faraday Soc., **55,** 418 (1959).
5. C.H. Bamford, A.D. Jenkins, *ibid.,* **59,** 530 (1963).
6. E.C. Chapin, G.E. Ham and C.K. Mills, J. Polym. Sci., **4,** 597 (1949).
7. F.M. Lewis, C. Walling, W. Cummings, E.R. Briggs and W. J. Wenisch, J. Am. Chem. Soc., **70,** 1527 (1949).
8. P.F. Onyon, J. Polym. Sci., **22,** 13 (1956).