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COPOLYMERIZATION OF ACRYLONITRILE AND CROTONIC ACID AND DETERMINATION OF REACTIVITY RATIOS

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Copolymerization of acrylonitrile and crotonic acid has been carried out at 60°C using benzoyl peroxide as initiator. Monomer reactivity ratios, r_A and r_B were determined using different methods. These values of r_A and r_B were then compared with the calculated values using Hammett equation.

The free radical type copolymerization of acrylonitrile and allyl acetate has been communicated earlier.[1] In this paper we present our findings on the benzoyl peroxide initiated copolymerization of acrylonitrile and crotonic acid carried out at 60°C. Different methods were adopted for the determination of monomer reactivity ratios. The values so obtained were then compared with the calculated value on the theoretical considerations.[2,3]

Experimental

The required amount of benzoyl peroxide (1%), acrylonitrile and crotonic acid was added in the reaction tube which was sealed at the constriction. The tubes were then heated at 60°C for 3 hr in a thermostatic-bath, then the seal was broken open and copolymer formed was washed with hexane.

The nitrogen of the copolymer sample was estimated by using Kjeldahl's method. The accuracy of our determination was ±0.53%.

Acrylonitrile (B.D.H.) was dried (Na_2SO_4), distilled at 76.2°C and stored in a dark container. Benzoyl peroxide of reagent grade was twice recrystallised. Crotonic acid (B.D.H.) and hexane (B.D.H.) were used without further purification. Laboratory grade *N*-*N'*,dimethyl foramamide was used after distillation.

Results and Discussion

The results (Table 1) show that the analysis of pure polyacrylonitrile gave 25.87% nitrogen while that of the product gave 17.5–23.5% nitrogen. The difference in percentage of nitrogen may be due to the attachment of crotonic acid in the polymer chain, suggesting that the product obtained is a copolymer. This is further supported by the fact that polyacrylonitrile is not soluble in cold dimethylformamide while the product obtained is soluble.

Monomer Reactivity Ratios.—By using intersection method of Mayo and Lewis,[4] the reactivity ratios of acrylonitrile, r_A and that of crotonic acid r_B were determined by the plot shown in Fig. 1. These are $r_A = 14$ and $r_B = 0$.

According to mole ratio method,[5] as shown in Fig. 2, $F(f-1)/f$ was plotted against F^2/f, where f represent copolymer ratio and F as monomer ratio. This gave $r_A = 11$ and $r_B = 0$.

The r_A and r_B values were also determined by using mole fraction method of Fineman and Ross,[6] where $f_A(1-2F_A)/(1-f_A)F_A$ was plotted against $f^2_A(F_A-1)/(1-f_A)^2F_A$, here f_A denotes the mole fraction of monomer in feed and F_A the mole fraction of monomer in the increment of copolymer formed at the start of reaction. The values obtained from Fig. 3 are $r_A = 11$ and $r_B = 0$.

The agreement in the values of r_A obtained by different methods are reasonably good. These have been shown in Table 2 for comparison. To have still a better estimate of reactivity ratios, the following relation[1] was used:

$$F_A = (\bar{r}_A f^2_A + f_A f_B)\,(\bar{r}_A f^2_A + 2 f_A f_B + \bar{r}_B f^2_A) \qquad (1)$$

Table 1.—Results from the Studies of Copolymerization of Acrylonitrile and Crotonic Acid at 60±0.1°C for 3 hr.

Expt. No.	Monomer in feed		Unreacted monomer		Nitrogen in the final product (%)
	Acrylonitrile, $[M_A]_0$ moles/l	Crotonic acid $[M_B]_0$ moles/l	Acrylonitrile, $[M_A]$ moles/l	Crotonic acid, $[M_B]$ moles/l	
1	1.800	9.984	1.239	9.804	17.5±0.53
2	3.430	8.459	2.157	8.233	20.5±0.53
3	5.058	7.263	3.021	7.031	22.3±0.53
4	6.668	6.162	3.859	5.974	23.5±0.53

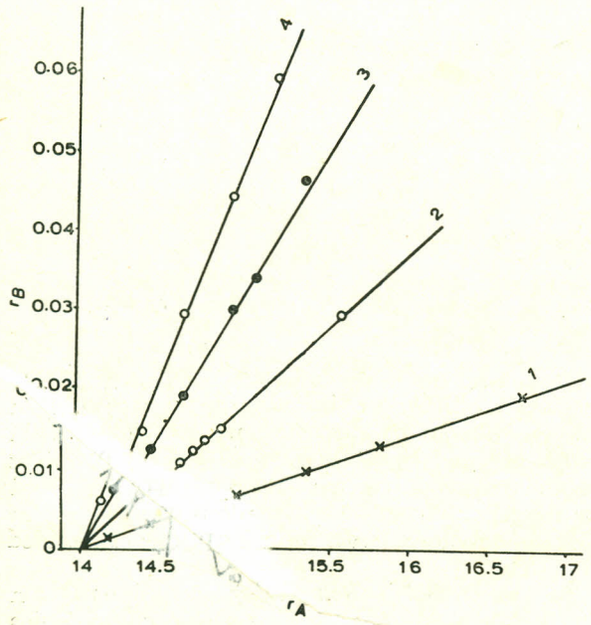

Fig. 1.—Mayo and Lewis plot of r_B against r_A for copolymerization of acrylonitrile and crotonic acid at 60°C.

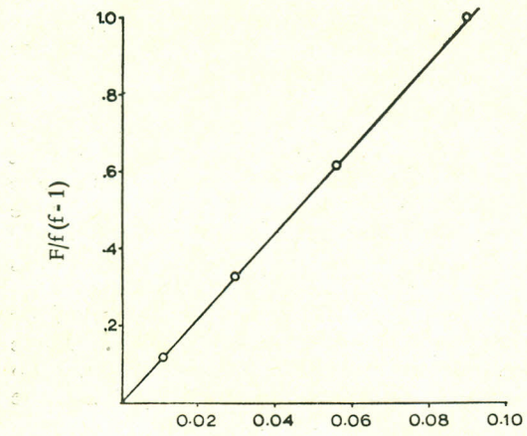

Fig. 2.—A plot of $F/f(f\text{-}1)$ versus $F2/f$ according to the mole ratio method to determine r_A and r_B values.

TABLE 2.—REACTIVITY RATIO VALUES r_A AND r_B, DETERMINED BY DIFFERENT METHODS FOR ACRYLONITRILE AND CROTONIC ACID COPOLYMERIZATION.

Method used	r_A	r_B
Mayo and Lewis method[4]	14.00	0
Mole ratio method[5]	11.00	0
Mole fraction method[6]	11.00	0
Hammett equation[2,3]	12.88	0.05

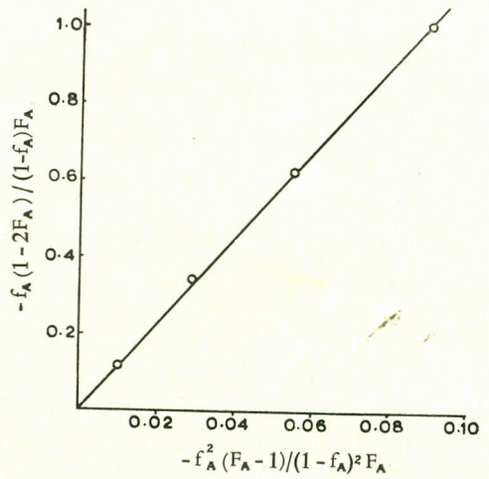

Fig. 3.—A plot of $f_A(1\text{-}2F_A)/(1\text{-}f_A)F_A$ against $f^2_A(F_A\text{-}1)$ $(1\text{-}f_A)^2F_A$ to determine r_A and r_B values.

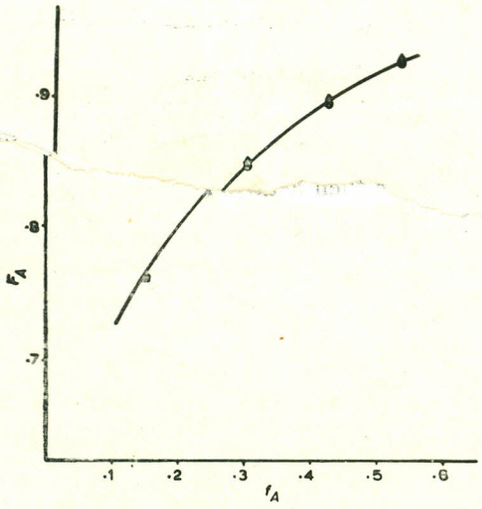

Fig. 4.—A plot of mole fraction of M_A in copolymer (F_A) against mole fraction of M_A in feed (f_A).

where $\bar{r}_A$ and $\bar{r}_B$ represent mean of the values obtained by three methods described above and f_B represent the mole fraction of monomer A and B in feed. The values of F_A thus obtained were plotted against f_A values as shown in Fig. 4, by solid circles. Similarly, F_A—f_A plots (shown by triangle) was also made with the aid of the following equation:

$$F_A=(M_A—M'_A)/[(M_A—M'_A)+(M_B—M'_B)] \quad (2)$$

where M_A and M_B represent monomers in feed while M'_A and M'_B indicate the unreacted monomers. The F_A versus f_A plots obtained by using equation(1), are in good agreement with the plots obtained by using equation(2). This further

TABLE 3.—REACTIVITY PARAMETERS USED IN CALCULATIONS.[3]

Monomer	α	β	σ
Acrylonitrile	−3	5.30	0.57
Crotonic acid	−2	3.62	0.38

suggests the reliability of our measurements described above.

The reactivity ratios were also calculated by using Hammett equation.[2,3] These are r_A= 12.88 and r_B=0.05. The values of the parameter used in the Hammett equation are shown in Table 3.

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References

1. S.A.K. Lodhi and A. Rasheed Khan, Pakistan J. Sci. Ind. Res., **13,** 358 (1970).
2. C.H. Bamford, A.D. Jenkins and R. Johnson, Trans. Faraday Soc., **55,** 418 (1959).
3. C.H. Bamford and A.D. Jenkins, Trans. Faraday Soc., **59,** 530 (1963).
4. F.R. Mayo and F.M. Lewis, J. Am. Chem. Soc., **66,** 1594 (1944).
5. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, New York, 1953), p. 186.
6. M. Fineman and S.D. Ross, J. Polymer Sci., **5,** 259 (1950).