FREE RADICAL INITIATED COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH TRICHLOROETHYLENE

R.A. Siddiqui and M.A. Quddus
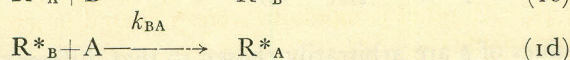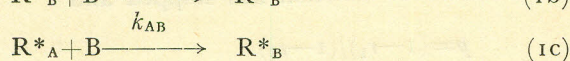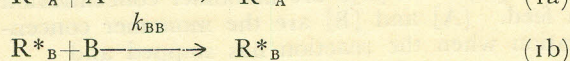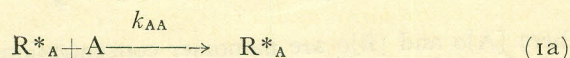
PCSIR Laboratories, Karachi 39

Maleic anhydride (A) has been copolymerized with trichloroethylene (B) as such and also in presence of diluents at 70°C, using benzoyl peroxide as initiator. The copolymer obtained at high maleic anhydride concentration was as black as poly(maleic anhydride), whereas the colour of the copolymer obtained at lower maleic anhydride content was brown. The monomer reactivity ratios $r_1 = 3.7 \pm 0.2$ and $r_2 = 0$, have been calculated by using both integrated and differential forms of copolymer equations. Kinetic considerations show that the rate of copolymerization in benzene is faster than in acetic anhydride.

It was generally considered that maleic anhydride as well as trichloroethylene does not homopolymerize by free radical mechanism.[1] However, recently this view has been disproved.[2,3] Maleic anhydride and trichloroethylene separately enter into copolymer reactions with a number of monomers.[4] Maleic anhydride in particular shows complete alternation of monomer units within a copolymer chain. The copolymerization reactions of maleic anhydride result in 1,2-addition to the olefin, therefore, the possibility of copolymerization of maleic anhydride with trichloroethylene has been investigated.

In terms of free radical mechanism, there are four possibilities involving the two monomeric reactants. These are:

$$R^*_A + A \xrightarrow{k_{AA}} R^*_A \qquad (1a)$$

$$R^*_B + B \xrightarrow{k_{BB}} R^*_B \qquad (1b)$$

$$R^*_A + B \xrightarrow{k_{AB}} R^*_B \qquad (1c)$$

$$R^*_B + A \xrightarrow{k_{BA}} R^*_A \qquad (1d)$$

A and B represent molecules of the two respective reactants. R^*_A and R^*_B are free radicals ending in A and B units respectively. The rate constants governing the addition of monomer molecules A and B to the growing chain are designated by k_{AA}, k_{BB}, k_{AB} and k_{BA}. The composition of the product of any copolymerization reaction will be governed by the ratios $r_1 = k_{AA}/k_{AB}$ and $r_2 = k_{BB}/k_{BA}$. These are known as monomer reactivity ratios.[5] Assuming steady state condition where the rate of creation of any type of radical R^*_A or R^*_B is equal to the rate of consumption, the following copolymerization equation[6] can be obtained.

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \cdot \frac{r_1[A] + [B]}{r_2[B] + [A]}$$

where $d[A]/d[B]$ is the monomer ratio in the increment of copolymer formed. [A] and [B] refer to the molar concentration of A and B.

Experimental

Materials.—Preparation of maleic anhydride:[7] A mixture of 200 ml xylene and 100 g maleic acid (commercial grade) was heated on an oil bath. The distillate obtained by heating up to 190°C was rejected. The receiver was then changed and the distillate boiling at 197–199°C (b.p. of maleic anhydride) was collected. The anhydride so obtained was recrystallized in chloroform.

Trichloroethylene (commercial grade) was distilled twice (b.p. 86.7°C). Benzoyl peroxide (BDH) was recrystallized twice from chloroform by the addition of methanol and was dried under vacuum at room temperature.

Procedure.—The required amounts of maleic anhydride, trichloroethylene and benzoyl peroxide were taken in Pyrex tubes. The tubes were flushed with nitrogen, sealed and heated in a thermostat bath at 70±0.1°C. After heating for 35 hr the tubes were cut and the contents of the tubes were taken in dry toluene. The insoluble copolymer was washed with sufficient toluene (300–400 ml), filtered and dried under vacuum at room temperature.

Analysis.—The copolymers were analysed for chlorine by Schoniger combustion method.[8]

Results and Discussion

The results of the copolymerization of maleic anhydride with trichloroethylene in benzene and in acetic anhydride solvents are shown in Table 1. It was observed that maleic anhydride was completely soluble in the reactants (experiment 1 and 2). After the desired time of heating some solid copolymer precipitated out. Since the copolymer under consideration contains large amount of maleic anhydride units, it was isolated with dry toluene according to the method adopted by Lang

TABLE 1.—COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH TRICHLOROETHYLENE IN PRESENCE OF DILUENTS. (2% w/w benzoyl peroxide, 35 hr, $70 \pm 0.1°C$)

Experiment	Maleic anhydride in feed mmole	Trichloroethylene in feed m-mole	Solvent (5 g)	Rate of entering of monomers in copolymer		%chlorine in copolymer
				Maleic anhydride $R_p \times 10^7$ $(ml^{-1}s^{-1})$	Trichloroethylene $R_p \times 10^8$ $(ml^{-1}s^{-1})$	
1	25.00	19.00	Benzene	7.0	6.3	8.5
2	25.00	19.00	Acetic anhydride	2.5	1.0	3.9

TABLE 2.—COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH TRICHLOROETHYLENE. (2% w/w benzoyl peroxide, 35 hr, $70 \pm 0.1°C$)

Experiment	Maleic anhydride in feed $[A]_o$ m-mole	Trichloroethylene in feed $[B]_o$ m-mole	Maleic anhydride unreacted $[A]$ m-mole	Trichloroethylene unreacted $[B]$ m-mole	% chlorine in copolymer
3	20.18	22.60	19.99	22.56	13.90
4	25.02	19.00	24.79	18.97	12.20
5	30.61	14.75	30.40	14.71	8.90
6	35.66	10.90	35.39	10.88	7.00

et al.[2] for the isolation of pure polymaleic anhydride. The colour of the reaction product in both these experiments (1 and 2) were remarkably different. It was brown when benzene was used as solvent, and almost black when acetic anhydride was used as solvent. The colour of the purified copolymers obtained in both of these experiments also bear the same gradation. It is seen from the Table 1 that the rate of copolymerization is faster in benzene than in acetic anhydride.

Another set of experiments having different monomeric concentrations in the feed, have been performed and the results are given in Table 2. It was observed that, as the concentration of maleic anhydride in feed was increased, the colour of the copolymer obtained deepened from brown to almost black. The colour of the pure poly (maleic anhydride) is black.[2] The filtrate, obtained after washing the copolymer with toluene, was evaporated. The residue thus obtained gave a test for chlorine. This suggested that the copolymer was partially soluble in toluene. Quantitative estimation of chlorine could not be made because of experimental difficulties encountered in it, such as presence of unreacted maleic anhydride in the residue and slow rate of evaporation of toluene. Furthermore, heating or warming to facilitate evaporation is not advisable because of possible decomposition.

With a view to evaluating the monomer reactivity ratios r_1 and r_2, equation 2 is integrated to get the following relation[5]

$$r_2 = \frac{\ln\frac{[B]_o}{[B]} - \frac{1}{p}\left[\ln\frac{1-p[A]/[B]}{1-p[A]_o/[B]_o}\right]}{\ln\frac{[A]_o}{[A]} + \left[\ln\frac{1-p\ [A]/[B]}{1-p\ [A]_o/[B]_o}\right]}$$

where $[A]_o$ and $[B]_o$ are monomer concentration in feed. $[A]$ and $[B]$ are the monomer concentration when the reaction has stopped and

$$p = (1-r_1)/(1-r_2)$$

Values of p are arbitrarily chosen so that different values of r_1 and r_2 are obtained in a significant region. A plot of r_1 versus r_2 (Fig. 1) gives a straight line for each experiment corresponding to Table 2. Generally two experiments performed under same conditions are needed to give two straight lines and their point of intersection determines the correct values of r_1 and r_2. However, more than two experiments are performed to calculate the range of error. When the reactivity ratio of one of the monomer is zero, say $r_2 = 0$, the straight lines should meet one another at a point on r_1 axis. Due to experimental errors, which are common in the free radical initiated reactions, the lines do not meet at a point, but are spread on the r_1 axis. The monomer reactivity ratios obtained by this plot for maleic anhydride and trichloroethylene are $r_1 = 3.7 \pm 0.2$ and $r_2 = 0$ respectively.
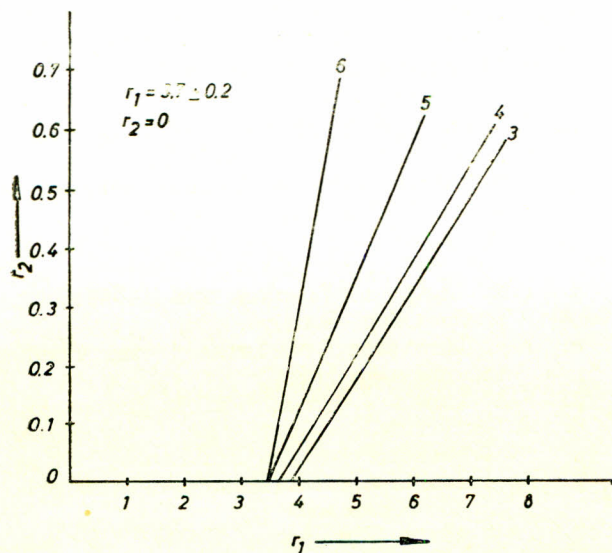
Fig. 1.—A plot of r_1 versus r_2 according to the method of Mayo and Lewis.[6] The numbering of the lines correspond to the experiments in Table 2.
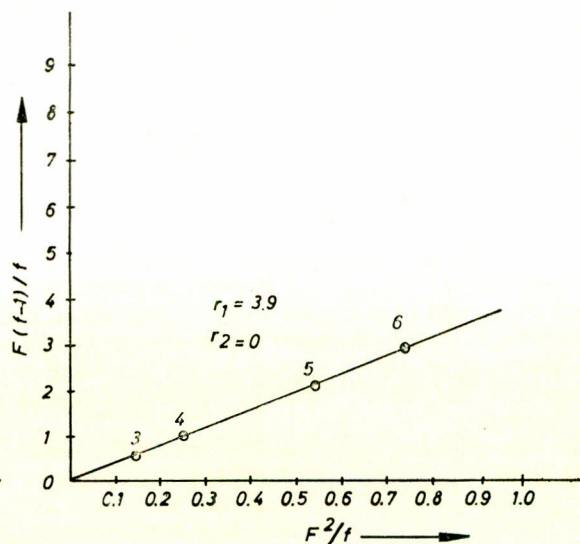

Fig. 2.—A plot of $F(f-1)/f$ versus F^2/f using the method of Fineman and Ross.[9] The numbering of the points correspond to the experiments in Table 2.
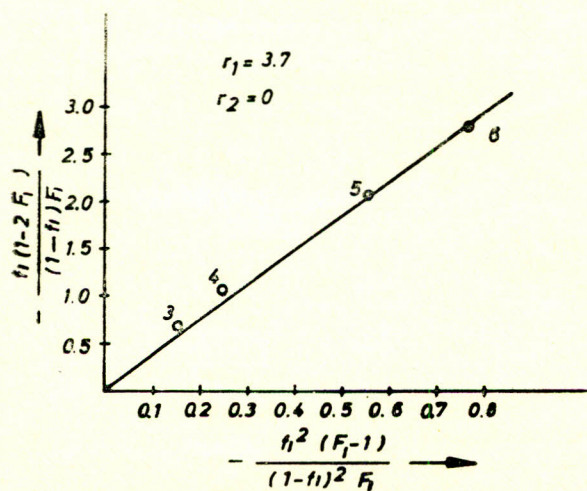

Fig. 3.—A plot of $f_1(1-2F_1)/(1-f_1)F_1$ against $f_1^2(F_1-1)/(1-f_1)^2F_1$ according to equation 5, by using the data given in Table 2.
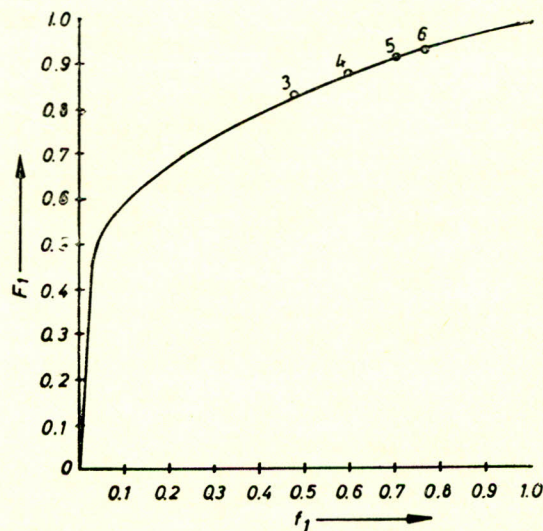

Fig. 4.—A plot of F_1 versus f_1 to obtain a theoretical curve. The points represent the value of $F1$ and f_1 calculated from the experimental data given in Table 2.

By substituting f for $d[A]/d[B]$ and F for $[A]/[B]$ in equation 2, Fineman and Ross[9] obtained the following relation

$$F(f-1)/f = r_1\frac{F^2}{f} - r_2 \tag{4}$$

If $r_1=0$ then the straight line represented by equation 4 should pass through origin and the slope would be equal to r_1. Fig. 2 gives $r_1=3.9$ and $r_2=0$.

The modified form of Fineman and Ross equation,[10] expressed in mole fraction of monomer A in feed $[f_A=(1-f_B)]$ and in copolymer formed $[F_A=(1-F_B)]$ is given by

$$f_1(1-2F_1)/(1-f_1)F_1 = r_1 f_1^2(F_1-1)/(1-f_1)^2F_1 + r_2 \tag{5}$$

The result of the plot of equation 5 in accordance with the data given in Table 2, is shown in Fig. 3 and the values of r_1 and r_2 given by this figure are

$r_1 = 3.7$ and $r_2 = 0$. The reactivity ratios determined by the above three methods are in good agreement.

Equation 5 with necessary rearrangement can be written as follows:

$$F_1 = (r_1 f_1^2 + f_1 f_2)/(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2) \qquad (6)$$

By inserting in this equation the mean values of r_1 and r_2 found by above methods and the values of f_1 and f_2, the corresponding values for F_1 can be calculated. A plot of F_1 versus f_1 gives a theoretical curve shown in Fig 4. Experimental values for F_1 and f_1 calculated from the data given in Table 2, fit well with the curve providing a reasonable test for the accuracy of the experiment performed.

In view of what has been said above, it is clear that benzoyl peroxide initiated free radical reaction between maleic anhydride and trichloroethylene results in a copolymer. The copolymerization reaction between these two monomers suggests that separate polymerization behaviour of individual monomer is a poor guide for the prediction of their copolymerization behaviour. In the present system $r_1 > 1$ and $r_2 < 1$, therefore the copolymerization system is non-azeotropic[11]

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