

COPOLYMERIZATION

Part II.*—Copolymerization of Acrylonitrile and Trichloroethylene

S.U. MULLIK† and M.A. QUDDUS

Physical Research Division, P.C.S.I.R. Laboratories, Karachi 32

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Acrylonitrile (A) has been copolymerized with trichloroethylene (B) using benzoyl peroxide as initiator at 75°C. The reactivity ratios found by the method of Mayo and Lewis are $r_A=62.1\pm 3.5$ and $r_B=0$. The theoretical curve obtained by using these values of reactivity ratios fits well to the experimental results. The determination of the mol wt and the chlorine analysis of the polymer indicate that the reaction product is a copolymer, not a telomer. Kinetic analysis has shown that at the initial stages of the reaction the time rate of acrylonitrile entering the copolymer is enormously faster than that of trichloroethylene whereas at the later stages when most of the acrylonitrile monomer is consumed both the time rates become comparable to each other. Further, evidence has been found that trichloroethylene homopolymerizes in the presence of benzoyl peroxide initiator at 75°C.

Introduction

Free radical induced binary copolymerizations of acrylonitrile and a number of other monomers have already been reported.^{1,2} Mention has been made of the reactivity ratios³ in the copolymerization of acrylonitrile (A) and trichloroethylene (B) at 60°C, but the experimental data on which the determination of the monomer reactivity ratios was based have not been published. In this paper the authors present the monomer reactivity ratios in the benzoyl peroxide initiated copolymerization of these two monomers at 75°C together with the rate of copolymerization as well as the homopolymerization of trichloroethylene initiated by the free radicals produced by benzoyl peroxide at 75°C.

Experimental

Material.—Acrylonitrile (B.D.H.) was dried over anhydrous sodium sulphate and distilled in an atmosphere of nitrogen. The middle fraction (b.p. 76.2°C, $D_4^{20}=0.806$) was collected and stored at 0°C in the dark.

Trichloroethylene (commercial grade) was distilled twice and the fraction boiling at 87°C was stored at 0°C in the absence of light. The density of the purified liquid was found to be 1.463 at 20°C.

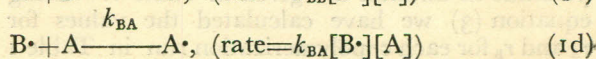
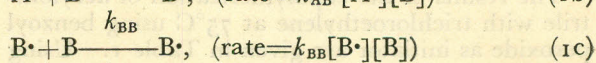
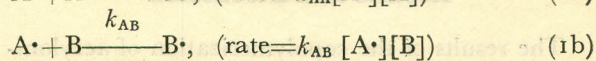
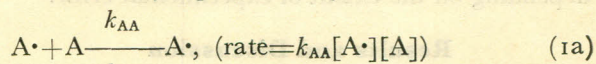
Benzoyl peroxide (B.D.H.) was recrystallized twice from chloroform by the addition of methanol. The recrystallized product was dried under vacuum at room temperature and stored at 0°C in the dark.

Procedure.—All the copolymerizations were performed in sealed Pyrex tubes. A weighed amount

of benzoyl peroxide (50 mg) was first poured through a funnel ending in a capillary into a Pyrex tube kept at 0°C. Then the required amounts of acrylonitrile and trichloroethylene were pipetted into the tube. The tube was flushed with nitrogen, carefully sealed and heated in a thermostat bath at $75.0\pm 0.1^\circ\text{C}$.

Analysis.—The copolymer was analysed for chlorine by burning a small quantity (40–50 mg) of it on a filter paper in oxygen (Schoniger combustion).⁴ 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 chlorine using Volhard's method.⁵ The accuracy of this method was checked by using the method of Carius.⁴ The deviation observed was within $\pm 0.5\%$.

Kinetic Equations for the Determination of Reactivity Ratios.—In a binary copolymerization there are two kinds of active centres which form at the growing ends of the polymer chains. The behaviour of an active centre depends solely upon the terminal monomer unit, and is independent of the length or overall composition of the growing polymer radicals. If A and B are the two monomers and A• and B• represent the chains ending in A and B units, respectively, the four growth reactions, which occur in such a case, may be schematically represented by



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where the first subscript with any specific rate constant, k_{AA} , k_{AB} , k_{BB} or k_{BA} refers to the reacting polymer radical and the second to the monomer. The symbol [] refers to the molar concentration of the species in the brackets (ml^{-1}). Assuming a steady state for any type of radical, $A\cdot$ or $B\cdot$, one can obtain the following copolymer composition equation^{6,7} by using the rate equations (1a-1d):

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \frac{r_A [A] + [B]}{r_B [B] + [A]} \quad (2)$$

where $d[A]/d[B]$ is the monomer ratio in the increment of copolymer formed, $[A]$ and $[B]$ are the instantaneous concentration of the two monomers, and $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$.

The integration⁷ of equation (2) with appropriate rearrangements gives

$$r_B = \frac{\ln \frac{[B]_0}{[B]} - \frac{1}{p} \ln \frac{1-p([A]/[B])}{1-p([A]_0/[B]_0)}}{\ln \frac{[A]_0}{[A]} - \ln \frac{1-p([A]/[B])}{1-p([A]_0/[B]_0)}} \quad (3)$$

where $[A]_0$, $[B]_0$ and $[A]$, $[B]$ represent the initial and the final monomer concentrations, respectively and $p = (1-r_A)/(1-r_B)$. Values of r_A and r_B are obtained from equation (3) by graphical method which has been developed by Mayo and Lewis. By this method values of p are arbitrarily chosen, by trial and error, to give points in a significant region for r_A and r_B . A plot of r_A as abscissa and r_B as ordinate is made and a straight line is obtained for each copolymerization experiment. Theoretically, two experiments will give two straight lines and their point of intersection will give the values of r_A and r_B . Practically, more than two copolymerization experiments are performed to find the range of experimental error. When the reactivity ratio⁸ of one of the monomers, for example, r_B is zero, the straight lines obtained from copolymerization experiments will be more or less parallel to one another and cut the r_A axis at different points depending on the extent of experimental error.

Results and Discussion

The results of the copolymerization of acrylonitrile with trichloroethylene at 75°C using benzoyl peroxide as initiator are given in Table I. Using equation (3) we have calculated the values for r_A and r_B for each copolymerization run in Table I

and plotted r_B against r_A in Fig. 1. Curves obtained from experiments run for 5 hr (except experiment 3) are meeting at one point on the r_A axis. Slight deviation has occurred in the case of the curve obtained from experiment number 3. This type of deviations which are common in free radical reactions may be due to the presence of trace impurities in the system. The values of r_A and r_B obtained from Fig. 1 are 62.1 ± 3.5 and 0, respectively, whereas the values reported by Mayo³ *et al.* are $r_A=67$ and $r_B=0$ at 60°C .

The compositions of the monomer feed and of the polymer formed as given in equation (2) may be expressed in mole fractions.^{2,9} If we let F_A represent the mole fraction of monomer A in the copolymer formed at a given stage in the polymerization, then

$$F_A = d[A] / d([A] + [B]) = 1 - F_B \quad (4a)$$

where F_B is the corresponding term for the monomer B. If f_A and f_B represent the mole fractions of monomers A and B in feed, i.e., $f_A = [A]/([A] + [B]) = 1 - f_B$, one can obtain from equation (2) and (4a),

$$F_A = (r_A f_A^2 + f_A f_B) / (r_A f_A^2 + 2f_A f_B + r_B f_B^2) \quad (4b)$$

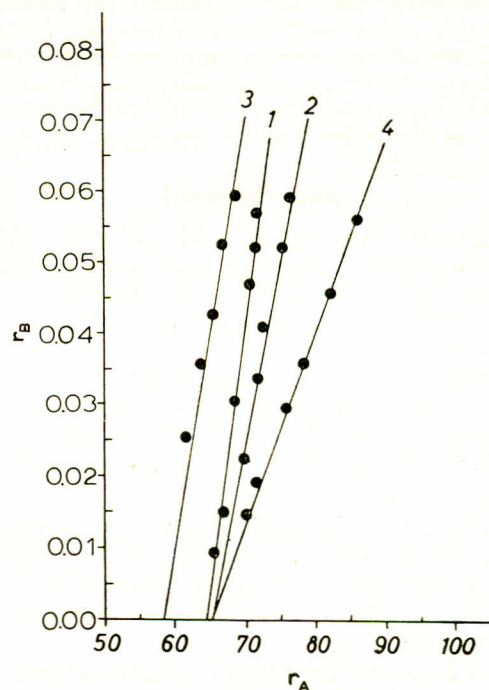


Fig. 1.—The plot of r_B against r_A by the method of Mayo and Lewis. The numbering of the lines (1,2,3, and 4) corresponds to that of the experiments in Table I.

The composition of the increment of copolymer formed at a monomer composition specified by $f_A=(1-f_B)$ has been calculated from equation (4b) using the values of monomer reactivity ratios ($r_A=62.1$ and $r_B=0$) obtained from Fig. 1 and the results given in Table 1. The values of F_A have been plotted against the corresponding values of f_A to obtain the theoretical curve shown in Fig. 2. The similar plot of the observed values of F_A and f_A obtained by the chemical analysis of the copolymers formed are shown in Fig. 2 by hollow circles (o). It is clear from Fig. 2 that the theoretical curve fits excellently to the experimental points. Thus the reliability of the values of r_A and r_B is confirmed.

In the present system the monomer reactivity ratios, r_A and r_B , are respectively greater and less than unity. Hence the copolymerization system is nonazeotropic.¹⁰ Since both r_A and $1/r_B$ are greater than unity, both polymer radicals prefer the same monomer, i.e., acrylonitrile monomer is more reactive than trichloroethylene monomer with respect to either radical. The present system is an extreme case of a nonazeotropic, binary copolymerization because acrylonitrile is about sixty-two times as reactive as trichloroethylene towards the acrylonitrile radical whereas the trichloroethylene radical prefers to add acrylonitrile monomer by a factor of infinity as compared with the addition of trichloroethylene. This

means that trichloroethylene radical does not add trichloroethylene monomer to any appreciable extent.

We have performed another set of experiments at fixed concentration of monomers and the initiator (Table 2). The results are shown in Fig. 3. The polymerization started immediately without showing any induction period and the copolymer settled out from the liquid monomer mixture at all stages of polymerization. In Fig. 3 the moles of acrylonitrile and of trichloroethylene entering the copolymer have been plotted against time. The rate of polymerization of acrylonitrile in bulk is very fast and irreproducible during

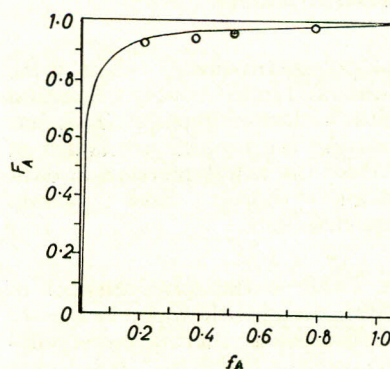


Fig. 2.—The mole fraction of acrylonitrile monomer in copolymer (F_A) has been plotted against the mole fraction of acrylonitrile monomer in feed (f_A). Hollow circles represent the experimental points (Table 1) but the curve is the plot of the theoretically calculated data.

TABLE 1.—COPOLYMERIZATION OF ACRYLONITRILE (A) WITH TRICHLOROETHYLENE (B) AT $75^\circ\text{C} \pm 0.1^\circ\text{C}$ USING 1% (W/W) BENZOYL PEROXIDE AS INITIATOR, THE DURATION OF THE REACTION BEING 5 HR.

Experiment no.	Acrylonitrile in feed, $[A]_0$ in millimoles	Trichloroethylene in feed, $[B]_0$ in millimoles	Acrylonitrile unreacted, $[A]$ in millimoles	Rate of polymerization of acrylonitrile, $R_p \times 10^5 (\text{ml}^{-1}\text{s}^{-1})$	Trichloroethylene unreacted, $[B]$ in millimoles	Rate of polymerization of trichloroethylene, $R_p \times 10^5 (\text{ml}^{-1}\text{s}^{-1})$	Chlorine in copolymer %
1	56.59	15.23	3.12	57.89	14.59	0.69	2.307
2	28.30	26.65	4.26	31.20	25.91	0.95	5.670
3	18.87	30.45	4.36	20.31	29.71	1.03	9.078
4	9.43	34.26	4.16	12.96	33.86	0.60	12.960

TABLE 2.—COPOLYMERIZATION OF 47.17 MILLIMOLES OF ACRYLONITRILE AND 19.04 MILLIMOLES OF TRICHLOROETHYLENE USING 50 MG BENZOYL PEROXIDE AS INITIATOR AT $75.0 \pm 0.1^\circ\text{C}$.

Experiment No.	Time of heating hr	Copolymer obtained g	% Chlorine in copolymer	$R_p \times 10^5$ for acrylonitrile $\text{ml}^{-1}\text{s}^{-1}$	$R_p \times 10^5$ for trichloroethylene $\text{ml}^{-1}\text{s}^{-1}$
5.	0.75	1.3469	2.360	188.40	2.28
6.	3.00	1.8453	2.553	63.06	0.83
7.	10.00	2.4550	3.073	25.53	0.41
8.	17.75	2.5408	3.546	14.79	0.27
9.	25.00	2.5424	4.710	10.35	0.26
10.	30.00	2.6188	5.052	8.64	0.24

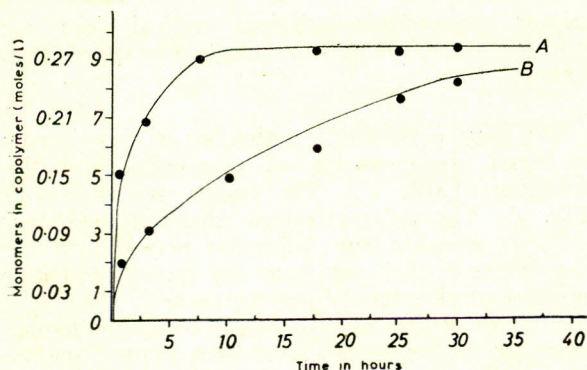


Fig. 3.—A plot of moles/litre of acrylonitrile (A) and of those of trichloroethylene (B) entering the copolymer against time in hours (Table 2). Outer scale of ordinate for trichloroethylene and inner scale for acrylonitrile.

the early stages of polymerization.¹¹ The same phenomenon was observed in the copolymerization of acrylonitrile with trichloroethylene. This has been ascertained during the preliminary stages of this work. As a result the copolymerization data obtained by durations shorter than 45 min have not been reported here.

It is seen from Table 2 that the amount of chlorine is increasing along with time, i.e., more and more trichloroethylene is entering the copolymer with the progress of the reaction. This is due to the fact that when two monomers are not identical in reactivity, the more reactive monomer enters the copolymer at a faster relative rate than the less reactive monomer and therefore the residual monomer mixture is progressively depleted of the more reactive monomer. At the later stages of the reaction the mixture has become richer in the less reactive component, which is reflected in the composition of the copolymer formed at this time. Thus the product of the reaction as a whole is a mixture of copolymer molecules of a wide range of chemical composition. This is further confirmed by the results shown in Table 1, where the rate of trichloroethylene entering the copolymer increases as the ratio of trichloroethylene to acrylonitrile is being increased.

The molecular weight of a copolymer sample obtained by the reaction of 47.17 millimoles of acrylonitrile and 19.04 millimoles of trichloroethylene in the presence of 1% (w/w) benzoyl peroxide initiator at 75°C for 10 hr was determined by using the following intrinsic viscosity mol wt relationship given by Onyon¹² for polyacrylonitrile.

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75} \quad (5)$$

where $[\eta]$, the intrinsic viscosity is expressed in dl/g. The intrinsic viscosity of the sample in *N,N'*-dimethylformamide at 25°C was found to be 1.59 dl/g. Thus the number average molecular weight, \bar{M}_n was about 64×10^3 . Hence the number average degree of polymerization is about 1208. Had the reaction been a telomerization due to chain transfer rather than a copolymerization, the above relation (5) would have held for the polymer quite satisfactorily, and consequently the polymer would have contained about 0.2% chlorine. Actually, the polymer sample was found to contain over 3% chlorine (Table 2). Moreover, like the other samples described in this paper the polymer sample was partly soluble in tetrahydrofuran (about 5%), whereas the polymer prepared under the same conditions in the absence of trichloroethylene was found to be completely insoluble in tetrahydrofuran. One can, therefore, conclude that the polymers obtained by the benzoyl peroxide initiated polymerization of acrylonitrile with trichloroethylene are copolymers rather than the telomeric homopolymers of acrylonitrile.

Action of Heat on the Copolymer.—At 120°C the copolymer (experiment 1, Table 1) changes its colour from white to light yellow after 31 hr of heating. At 200°C it turns black within 2½ hr. Above 265°C the copolymer decomposes with the formation of insoluble black solid products. The cause of this coloration in the copolymer is believed to be due to the elimination of HCN from the macromolecular chain resulting in the formation of long chain conjugated double bonds wherein the depth of colour depends on the length of conjugation, and the formation of insoluble products is the result of intermolecular cross-linking of the copolymer chains.¹³

Polymerization of Trichloroethylene.—It is generally believed that monomers^{14,15} like trichloroethylene, tetrachloroethylene, etc. do not homopolymerize. This has been attributed to the fact that head-to tail joining between two monomer units is hindered due to the steric effect of the adjacent bulky chlorine atoms. However, our experiments indicate that some polymer is indeed formed when trichloroethylene is heated at 75°C with 1% (w/w) benzoyl peroxide, although the degree of polymerization appears to be very low. The formation of polymer has been detected by the measurement of viscosity change. The procedure of charging and heating the reaction tubes was, as described in this paper, for the copolymerization of this monomer and acrylonitrile. The results are given in Table 3. In the case of experiment 13 (Table 3), the product after taking the viscosity measurement was evaporated and a

TABLE 3.—VISCOSITY MEASUREMENTS TO FOLLOW THE HOMOPOLYMERIZATION OF TRICHLOROETHYLENE

Experiment No.	Temp. (°C) of viscosity measurement	Trichloroethylene g	Benzoyl peroxide g	Duration of heating at 75°C hr	Viscosity in centistokes
11.	27	21.75	0.0	0.0	0.3471
12.	27	21.75	0.2175	0.0	0.3522
13.	27	21.75	0.2175	15.0	0.4139
14.	25	21.75	0.0	0.0	0.3556
15.	25	21.75	0.2175	0.0	0.3625
16.	25	21.75	0.2175	13.5	0.4156
17.	25	21.75	0.2175	13.5	0.4184

brownish oily liquid was left. A portion of the oily liquid, on warming up, boiled above 90°C, with decomposition giving dark brown product. However, the other portion, on evaporating under low pressure, gave a small amount of brownish solid product. These observations have compelled us to believe that under the above mentioned reaction conditions trichloroethylene polymerizes giving unstable low mol wt polymer. Further experiments in this line are in progress.

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