

## COPOLYMERIZATION

## Part III.—Copolymerization of Acrylonitrile and Tetrachloroethylene

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A study has been made of the copolymerization of acrylonitrile and tetrachloroethylene in the presence of 1% (w/w) benzoyl peroxide at 50 and 75°C. The rate of copolymer formation is found to increase with the increase of acrylonitrile concentration. The increase in tetrachloroethylene concentration does not appreciably increase the incorporation of chlorine in the resulting copolymer. The monomer reactivity ratios at 75°C are  $r_1=456\pm 70$  and  $r_2=0$ . The mol wt determination of a copolymer sample has shown that the polymerization product is a copolymer not a telomer. The copolymer decomposes into insoluble black products between 200 and 218°C without showing any softening point.

**Introduction**

The copolymers<sup>1</sup> of acrylonitrile are industrially very useful. The largest use of acrylonitrile is in the synthetic rubber industry where it is copolymerized with butadiene to obtain the well-known Buna-N and other nitrile rubbers. The materials made of nitrile rubbers are very durable because of their high tensile and impact strengths and high resistance to heat and many chemicals. In recent years the use of acrylonitrile in the synthetic fibre and plastic industries has grown enormously. The high nitrile content copolymers of acrylonitrile are useful materials for the production of fibres having good resistance to stretch, heat, microorganisms and insects. The nitrile containing plastics have excellent dielectric properties, light stability and high softening temperatures.

A knowledge of the usefulness of acrylonitrile copolymers had led us to study the unexplored copolymerization of this monomer with other monomers. The free radical<sup>2</sup> or ionic polymerization<sup>3</sup> of acrylonitrile monomer is so fast a reaction that the results at the initial stages of polymerization are irreproducible. Similar results have been observed by the workers<sup>4,5</sup> of this Laboratory in the copolymerization of this monomer with a number of other monomers. Consequently, in most of the cases we have not reported the results of monomers conversion below 10%. The purpose of this work is to investigate the hitherto unreported kinetics of the copolymerization of acrylonitrile ( $M_1$ ) and tetrachloroethylene ( $M_2$ ) at 50 and 75°C and to study the properties of the copolymers formed. In addition, we have reported the monomer reactivity ratios in the copolymerization at 75°C. The monomer reactivity ratios in this system has already been reported by Doak<sup>6</sup> from a single ex-

periment at 60°C, who, however, failed to note the duration of the polymerization and the range of error involved in the determination of monomer reactivity ratios. Our results at 75°C do not differ much from Doak's results at 60°C as expected but we have been able to point out the range of error involved in the determination of the monomer reactivity ratios in this copolymerization system.

**Experimental**

*Materials.*—Acrylonitrile (B.D.H.) was dried over  $\text{Na}_2\text{SO}_4$  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.

Tetrachloroethylene (George and Becker) was fractionally distilled in an atmosphere of nitrogen and the middle third (b.p. 121°C,  $D_4^{15^\circ}=1.631$ ) was stored at 0°C in the dark.

Benzoyl peroxide (B.D.H.) was twice recrystallized from chloroform by the addition of methanol and dried under vacuum at the room temperature.

Both laboratory grade methanol (B.D.H.) and dimethyl formamide (B.D.H.) were used after distillation.

*Procedure.*—Required amounts of acrylonitrile, tetrachloroethylene and benzoyl peroxide were taken in Pyrex tubes. These tubes with their contents were cooled to 0°C while being flushed with nitrogen and then sealed carefully. Finally, the sealed tubes were heated at constant temperature in a thermostat bath. After the desired time of heating the tubes were cut open and the contents were individually washed with methanol and dried under vacuum at the room temperature to constant weight. In the calculation of all experimental data, the density of acrylonitrile and that of tetrachloroethylene were taken as

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0.8004 and 1.6004 g/ml, respectively, at the room temperature.

*Analysis.*—Chlorine was estimated by burning the copolymer samples in oxygen as described earlier.<sup>4</sup> The resulting products were absorbed in alkali solutions containing hydrogen peroxide and titrated using the method of Volhard.<sup>7</sup>

The UV absorption spectra of the copolymer in solutions of dimethyl formamide were measured by using a Unicam SP-500 spectrophotometer. Viscosity measurements were made by the use of a simple Oswald viscometer.

### Results and Discussion

Results of the copolymerization of acrylonitrile and tetrachloroethylene at 50°C are given in Table 1 and those at 75°C in Tables 2 and 3. The concentration of acrylonitrile in the copolymerization experiments shown in Table 1 was in the range of 20 to 80% (w/w) whereas that given in Table 2 and 3 was in the range of 5 to 40% (w/w).

*General Kinetics.*—The rates of polymerization of acrylonitrile,  $R_p \times 10^5$  moles/l/sec, have been plotted against the concentrations of acrylonitrile, moles/l, in Fig. 1. In all the systems the rate of polymerization increases with the increase of acrylonitrile concentration. Each system appears to

behave like a solution polymerization system where the rate of polymerization is affected by the dilution effect. In most cases of solution polymerization<sup>8</sup> the rate decreases with the increase of solvent concentration but in some cases the rate increases with the increase of solvent concentration, reaches a maximum value, and then begins to decrease with further dilution. The cause of decrease in the rate of polymerization with dilution is a general one because mechanistically the rate of free radical initiated polymerization,  $R_p$ , is directly proportional to the first power of monomer concentration,  $[M]$  and 0.5 power of initiator concentration but the contrary fact that rate increases with dilution has been attributed to the increase in initiator efficiency in certain solvents.<sup>9</sup>

The plot of the variation of chlorine content in the copolymer against the mole ratio of tetrachloroethylene to acrylonitrile for all sets of experiments has been shown in Fig. 2. The rate of chlorine being embedded in the copolymer increases with the increase in tetrachloroethylene concentration. However, the extent of increase is not uniform throughout the whole range of experiments in any system. The reason of such an unusual behaviour is not clear to us. Tetrachloroethylene does not homopolymerize. It is generally believed that this is due to steric hindrance<sup>10</sup> caused by the bulky chlorine atoms on both the carbon atoms. However, tetrachloro-

TABLE 1.—COPOLYMERIZATION OF ACRYLONITRILE (AN) AND TETRACHLOROETHYLENE (TCE) FOR 5 HR USING 50 MG BENZOYL PEROXIDE AT 50.0 ± 0.1°C

| Experiment No. | Monomers in feed |                | Copolymer obtained g | % Chlorine in copolymer | Rate of polymerization of      |                                   |
|----------------|------------------|----------------|----------------------|-------------------------|--------------------------------|-----------------------------------|
|                | AN millimoles    | TCE millimoles |                      |                         | AN $R_p \times 10^5$ moles/sec | TCE $R_p \times 10^5$ moles/l/sec |
| 1              | 18.87            | 24.10          | 0.450                | 1.65                    | 12.45                          | 0.12                              |
| 2              | 28.30            | 21.09          | 0.720                | 1.56                    | 18.30                          | 0.11                              |
| 3              | 47.17            | 15.06          | 1.249                | 1.30                    | 27.58                          | 0.14                              |
| 4              | 75.48            | 6.00           | 1.768                | 1.14                    | 33.14                          | 0.14                              |

TABLE 2.—COPOLYMERIZATION OF ACRYLONITRILE AND TETRACHLOROETHYLENE FOR 5 HR USING 50 MG BENZOYL PEROXIDE AT 75.0 ± 0.1°C

| Experiment No. | Monomers in feed |                | Copolymer obtained g | % Chlorine in copolymer | Rate of polymerization of        |                                   |
|----------------|------------------|----------------|----------------------|-------------------------|----------------------------------|-----------------------------------|
|                | AN millimoles    | TCE millimoles |                      |                         | AN $R_p \times 10^5$ moles/l/sec | TCE $R_p \times 10^5$ moles/l/sec |
| 5              | 4.72             | 28.62          | 0.192                | 1.66                    | 6.03                             | 0.03                              |
| 6              | 9.43             | 27.11          | 0.370                | 1.63                    | 11.12                            | 0.08                              |
| 7              | 14.16            | 25.61          | 0.563                | 1.60                    | 16.08                            | 0.09                              |
| 8              | 18.87            | 24.10          | 0.737                | 1.59                    | 20.33                            | 0.12                              |
| 9              | 23.85            | 22.59          | 0.962                | 1.56                    | 25.51                            | 0.16                              |
| 10             | 28.30            | 21.09          | 1.106                | 1.53                    | 28.09                            | 0.16                              |
| 11             | 37.73            | 18.01          | 1.478                | 1.42                    | 35.00                            | 0.19                              |

TABLE 3.—COPOLYMERIZATION OF ACRYLONITRILE AND TETRACHLOROETHYLENE FOR 3.75 HR USING 50 MG BENZOYL PEROXIDE AT  $75.0 \pm 0.1^\circ\text{C}$ 

| Experiment No. | Monomers in feed          |                            | Copolymer obtained g | % Chlorine in copolymer | Monomers unreacted      |                          | Rate of polymerization of        |                                   |
|----------------|---------------------------|----------------------------|----------------------|-------------------------|-------------------------|--------------------------|----------------------------------|-----------------------------------|
|                | AN, $[M_1]_0$ milli-moles | TCE, $[M_2]_0$ milli-moles |                      |                         | AN, $[M_1]$ milli-moles | TCE, $[M_2]$ milli-moles | AN $R_p \times 10^5$ moles/l/sec | TCE $R_p \times 10^5$ moles/l/sec |
| 12             | 4.72                      | 28.62                      | 0.170                | 1.63                    | 1.57                    | 28.60                    | 7.12                             | 0.04                              |
| 13             | 9.43                      | 27.11                      | 0.320                | 1.63                    | 3.51                    | 27.07                    | 12.81                            | 0.10                              |
| 14             | 14.16                     | 25.61                      | 0.558                | 1.60                    | 3.86                    | 25.54                    | 21.37                            | 0.13                              |
| 15             | 16.97                     | 24.70                      | 0.645                | 1.60                    | 5.03                    | 24.63                    | 24.10                            | 0.15                              |
| 16             | 18.87                     | 24.10                      | 0.739                | 1.59                    | 5.18                    | 24.02                    | 27.19                            | 0.16                              |

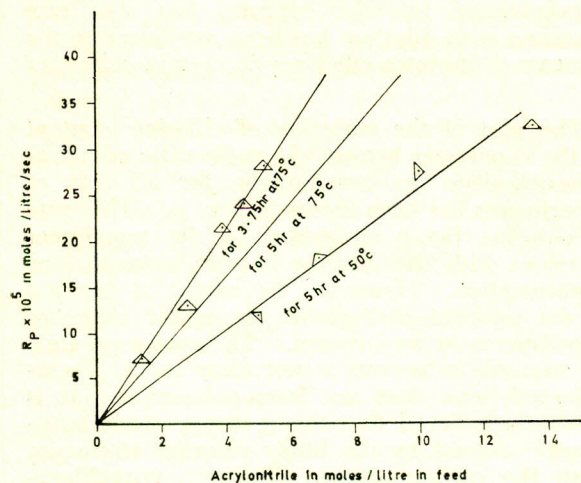
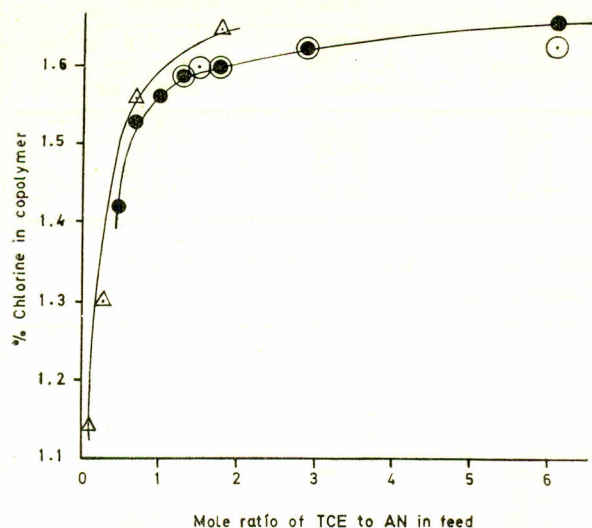
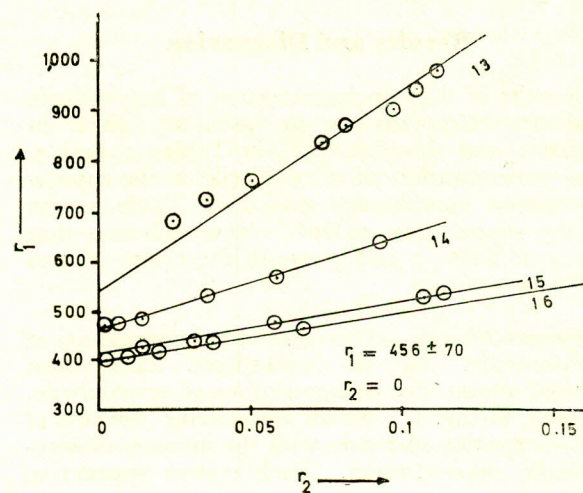


Fig. 1.—Rate of polymerization of acrylonitrile in tetrachloroethylene.


 Fig. 2.—A plot of % chlorine in copolymer against the mole ratio of tetrachloroethylene (TCE) to acrylonitrile (AN).  $\Delta$  at  $50^\circ\text{C}$  for 5 hr,  $\bullet$  at  $75^\circ\text{C}$  for 5 hr and  $\circ$  at  $75^\circ\text{C}$  for 3.75 hr.

 Fig. 3.— $r_1$  has been plotted against  $r_2$  in the benzoyl peroxide initiated copolymerization of acrylonitrile ( $M_1$ ) and tetrachloroethylene ( $M_2$ ) at  $75^\circ\text{C}$ . The numbering of the lines corresponds to that of the experiments in Table 3.

ethylene<sup>6</sup> has been shown to copolymerize with vinyl acetate giving a copolymer containing chlorine to the extent of 8% and with styrene forming a copolymer which contains over 2% chlorine. Unfortunately, these studies are not sufficient to predict the kinetic behaviour of this compound. No other copolymerization study of tetrachloroethylene is known. However, this point will be further discussed in connection with the mol wt of the copolymer.

*Monomer Reactivity Ratios.*—The monomer reactivity ratios  $r_1$  and  $r_2$  are determined by using the integrated form<sup>11</sup> of the copolymerization composition equation. The detailed procedure of the method used has been discussed in the earlier papers<sup>4,5</sup> of this series. In Fig. 3, the  $r_1$  values representing the monomer reactivity ratios of acrylonitrile have been plotted against the  $r_2$  values representing those of tetrachloroethylene.

Results of experiments 13 to 16 of Table 3 have been shown in Fig. 3, where each straight line represents one copolymerization experiment. The plot of other experimental results (experiment 12 of Table 3 and experiments of Table 1 and 2) are not shown here because the range of error in the monomer reactivity ratios given by their plot is found to be beyond the limit accepted by the method of Mayo and Lewis.<sup>11</sup> This is mainly due to high conversions of monomers into copolymers and partly due to inaccuracy involved in the chlorine analysis.<sup>4,8</sup> However, the monomer reactivity ratios calculated from the plot in Fig. 3 are  $r_1=456 \pm 70$  and  $r_2=0$ , whereas the results obtained by Doak<sup>6</sup> are  $r_1=470$  and  $r_2=0$  at 60°C.

Since one reactivity ratio is greater than unity and the other is less than unity, the copolymerization system of acrylonitrile and tetrachloroethylene is nonazeotropic.<sup>12</sup> As both  $r_1$  and  $1/r_2$  are greater than unity, both radicals prefer the same monomer i.e. acrylonitrile. Acrylonitrile is about 456 times as reactive as tetrachloroethylene towards the polyacrylonitrile radical but polytetrachloroethylene radicals prefers to adding acrylonitrile monomer by a factor of infinity. Hence polymerization of a mixture of similar amounts of acrylonitrile and tetrachloroethylene gives an initial product which is virtually pure polyacrylonitrile. When most of acrylonitrile monomer is consumed, a copolymer containing comparable proportion of tetrachloroethylene will be formed.

*Molecular Weight.*—The viscosity of the copolymer solutions in dimethyl formamide was measured at 25°C. The number average molecular weight  $\bar{M}_n$  of a copolymer sample (experiment 16, Table 3) was determined by using the following relationship of intrinsic viscosity  $[\eta]$  and number average molecular weight given by Onyon<sup>13</sup> for polyacrylonitrile.

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

The molecular weight of the sample was found to be 31000,  $[\eta]$  being 0.906 decilitre/g. If the sample would have been pure polyacrylonitrile chains in telomeric form,



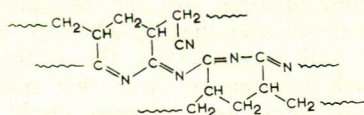
the above relationship between intrinsic viscosity and mol wt would have held and accordingly the sample would have contained about 0.5% chlorine. Actually the sample was found to contain 1.59% chlorine. Hence the sample is a

copolymer. However, the possibility of telomerization to some extent due to chain transfer to tetrachloroethylene could not be ruled out. As a general rule, with the increase of tetrachloroethylene concentration the rate of chain transfer to this monomer and that at which it enters the copolymer will increase but the chain transfer reaction will incorporate only one molecule of tetrachloroethylene per polymer chain whereas the copolymerization will introduce a number of these molecules in a polymer chain, the extent of which will be defined by various kinetic factors of the copolymerization system.<sup>14</sup> The enhanced chain transfer at higher concentration of tetrachloroethylene may be the major cause while the curves in Fig. 2 are not having a uniform slope throughout the whole range of monomer ratios. This effect is not noticeable in the curves of Fig. 1, since the rate at which acrylonitrile monomer is entering the copolymer is enormously high in comparison to the combined rates at which tetrachloroethylene enters the growing polymer chain by chain transfer as well as by copolymerization.

*Melting Point and Absorption Spectra.*—All the copolymer samples mentioned in Tables 1, 2 and 3 were white powdery substances which were easily soluble in dimethyl formamide on warming at about 70°C. After heating for 45 hr at 122°C in air, a copolymer sample appeared to retain its whiteness but it had lost about 1% weight, and about 5% of the sample became insoluble in dimethyl formamide. Moreover, a 0.1% solution in dimethyl formamide of the heated copolymer sample gave an absorption peak at 5300Å whereas a solution of the same strength in the same solvent of the unheated copolymer was 100% transparent at this wavelength. However, the copolymer was found to decompose into dark black products between 200 and 218°C in the presence of air, apparently, without showing any softening point. The decomposed products were mostly insoluble in dimethyl formamide. Polyacrylonitrile prepared from acrylonitrile monomer in the absence of tetrachloroethylene under the conditions described in this paper was also a white powdery substance which decomposed around 165°C giving mostly insoluble black products. Above 200°C the copolymer began to turn yellow, then became brown and finally black.

It has been shown by Grassie and Hay<sup>15</sup> that at temperatures of 140 to 200°C in the absence of oxygen polyacrylonitrile or its binary copolymer with methyl vinyl ketone, methyl methacrylate, methacrylonitrile or styrene becomes discoloured and insoluble due, respectively, to the intramolecular and intermolecular rearrangements of nitrile

groups in the polymer chains. The resulting structure from polyacrylonitrile could be depicted as shown below:



The coloration<sup>16</sup> of polymers by heat or radiation is, usually, attributed to the formation of long chain conjugated double bonds. The possibility of such a mechanism leading to the coloration of acrylonitrile homopolymer or copolymer is ruled out from the fact that there is no loss in weight of the polymer or the copolymer at temperatures below 200°C. Above 200°C it loses HCN even in the absence of oxygen.

In the present case where the copolymer contains, on the average, 3 to 4 tetrachloroethylene units per polymer chain of about 584 acrylonitrile units, the coloration of the copolymer above 200°C in the presence of air is likely to be due mostly to the formation of long chain conjugated double bonds by the loss of HCN. The loss in weight of the copolymer has been detected even at 122°C. The insolubility of the heated copolymer could have been caused by the cross-linking of the degraded copolymer and the intermolecular rearrangements of the nitrile groups of the undegraded copolymer. Moreover, in the presence of air the copolymer might have undergone chain scission and oxidation reactions in addition to other reactions already discussed.

## References

1. *Encyclopaedia of Polymer Science and Technology* (Interscience, New York, 1964), Vol. 1, p. 413.
2. C.H. Bamford, W.G. Barb, A.D. Jenkins and P.F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanisms* (Butterworths & Co., London, 1958), p. 104.
3. M.L. Miller, *J. Polymer Sci.*, **56**, 203 (1962).
4. S.U. Mullik, S.A.A. Chishti, S.B. Kapadia, *Pakistan J. Sci. Ind. Res.*, **11**, 125 (1968).
5. S.U. Mullik and M.A. Quddus, *Pakistan J. Sci. Ind. Res.*, **12**, 181 (1969).
6. K.W. Doak, *J. Am. Chem. Soc.*, **70**, 1525 (1948).
7. A.I. Vogel, *A Textbook of Quantitative Inorganic Analysis* (Longmans, Green and Co., London, 1947), p. 322.
8. M.H. George and P.F. Onyon, *Trans. Faraday Soc.*, **59**, 1390 (1963).
9. G.M. Burnett, W.S. Dailey and J.M. Pearson, *Trans. Faraday Soc.*, **61**, 1216 (1965).
10. T. Alfrey, Jr., J. J. Bohrer and H. Mark, *Copolymerization* (Interscience, 1952), p. 45.
11. F.R. Mayo and F.M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
12. Ref. 2, p. 156.
13. P.F. Onyon, *J. Polymer. Sci.*, **22**, 13 (1956).
14. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, New York, 1953), p. 178.
15. N. Grassie and J. N. Hay, *J. Polymer Sci.*, **56**, 189 (1962).
16. H.H.G. Jellinek, *Macromolecular Chemistry I.U.P.A.C.*, (Butterworths & Co., London, 1962), p. 419.