

# Aspects of the Kinetics of the Radiation-Induced Polymerization of Acrylonitrile in Dimethylformamide

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## Synopsis

The radiation-induced homopolymerization of acrylonitrile (AN) in dimethylformamide (DMF) has been followed in detail over a range of monomer concentrations. In all cases a short induction period was observed which was equivalent to  $1.6 \times 10^4$  rad. The initial rates of polymerization for solutions of AN in DMF of mole fraction ( $X$ ) of 0.33, 0.20, and 0.10 are  $1.44 \times 10^{-5}$ ,  $7.23 \times 10^{-6}$ , and  $2.79 \times 10^{-6}$  mole/dm<sup>3</sup> rad, respectively. Deviations of the polymerization pathway from the standard unity in monomer dependence are examined in terms of radical production ratios to the monomer and the solvent ( $\Phi_M/\Phi_S$ ) and the polymer together with the solvent ( $\Phi_P/\Phi_S$ ), for various mole fractions of AN in DMF. Thus, an indirect route to  $G_{\text{radical}}$  (events) is provided together with the corresponding  $k_p^2/k_t$  values.

## INTRODUCTION

Considerable interest has been shown in the radiation-induced polymerization of AN in aqueous<sup>1-5</sup> and nonaqueous media.<sup>6-9</sup> This article is an extension of our interest in self-colored polymers based on PAN<sup>10,11</sup> and on the alkali-induced degradation of the homopolymer.<sup>12</sup> We are equally concerned with the origin of color with degraded PAN, whether thermally or alkali induced,<sup>13</sup> though these findings will be presented in another publication. Whereas polymerization of AN, in bulk or aqueous media or in any solvent for the monomer which is a nonsolvent for PAN, is autocatalytic, that in DMF is reasonably free from such effects except at very high conversion rates.<sup>14,15</sup>

We are interested in the relative contribution to the homopolymerization reaction made by various radical species in the system, arising as a result of exposure to high-energy radiation.

## EXPERIMENTAL

Analytical-grade AN was washed with 1M sulfuric acid, sodium carbonate, and then washed thoroughly with water before drying over anhydrous calcium chloride and vacuum distilling at room temperature, only the middle fraction being taken. This fraction, still under vacuum, was exposed to  $3 \times 10^3$  rad of  $\gamma$ -radiation from a <sup>60</sup>Co facility which gave 2% homopolymerization. The residual monomer was again distilled at room temperature, under vacuum, to separate it from the polymer and any impurity. The first and last 10% were discarded.

DMF was distilled under nitrogen from phosphorus pentoxide. It was stored in sealed containers in the dark at 273 K and was never kept for more than three days after distillation.

Solutions of AN in DMF were assembled gravimetrically in tared flasks which were immediately stoppered. The density of each mixture at 293 K was measured separately. Known volumes of solution were syringe-pipetted into ampoules, subjected to three freeze/thaw cycles under vacuum before isolating at  $1.33 \times 10^{-2} \text{ N/m}^2$ .  $\gamma$  radiation was used in initiation, the dose rate being monitored by Fricke dosimetry. The dose rate was correlated for the different adsorption coefficients of water (where relevant), DMF, and AN (1:0.986 and 0.950, respectively).

The polymer solution was poured into ten times its own volume of rapidly stirring cold water. PAN was filtered on No. 4 porosity sintered crucibles, washed with water and then methanol, and dried under vacuum at 323 K. The characteristics of the monomer solutions are shown in Table I.

## RESULTS AND DISCUSSION

Figure 1 shows the extent of homopolymerization related to the radiation dose. It is more convenient to express periods in rads rather than time units, as this makes the comparison of results, obtained at slightly different dose rates, much easier. Thus, rates of homopolymerization are expressed as moles of AN converted to PAN/dm<sup>3</sup>/rad<sup>1</sup>. In the foregoing sections, primed symbols, for example,  $R'_p$ , will be used for such quantities while the unprimed  $R_p$  will be used for rate expression based on time units. The slopes from Figure 1 are compared with the corresponding conversion to PAN and are shown in Figure 2. Extrapolation of the data in Figure 2 to zero conversion gives the initial rates of polymerization ( $R_p^1$ )<sub>0</sub>. These have been calculated as 14.4, 7.23, and 2.79 (all  $\times 10^{-6}$ ) mole/dm<sup>3</sup> rad for mole fractions  $X_{AN}$  of 0.33, 0.20, and 0.10, respectively.

According to simple kinetic theory,

$$R_p = \frac{k_p[M]R_i^{1/2}}{(2k_t)^{1/2}} \quad (1)$$

and the rate of polymerization should be directly proportional to the monomer concentration (dashed lines in Fig. 2). In this work the experimental rates fall well below direct proportionality. Thus, the overall rate must depend on some power  $>1.0$ , i.e.,

$$R_p = \frac{k_p[M]^x R_i^{1/2}}{(2k_t)^{1/2}} \quad \text{where } x > 1 \quad (2)$$

or the rate of initiation may fall as the monomer concentration falls. Conventionally, the order of reaction may be found by comparing the dose required to convert a given fraction of monomer to polymer for different initial monomer

TABLE I  
Characteristics of Monomer Solution

Mole fraction $X_{AN}$	Density, kg/dm <sup>3</sup>	AN, mole/dm <sup>3</sup>	DMF, mole/dm <sup>3</sup>
A 0.33	0.9086	4.566	9.132
B 0.20	0.9260	2.684	10.736
C 0.10	0.9377	1.321	11.889

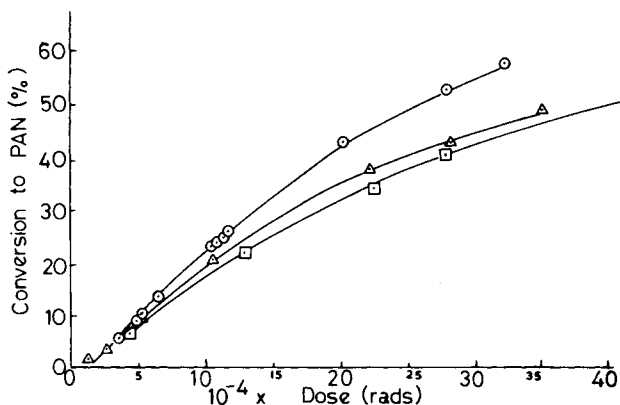


Fig. 1. Variation in the extent of polymerization to PAN with increasing dose for various initial bulk monomer/DMF compositions. Mole ratio AN:DMF: (○) 1:2; (△) 1:4; (□) 1:9.

concentrations. This was found to be unsatisfactory for the present data, possibly because the rate of initiation is different in each case, depending on the composition of the solution.

An alternative approach, using only a single concentration of solvent, is to

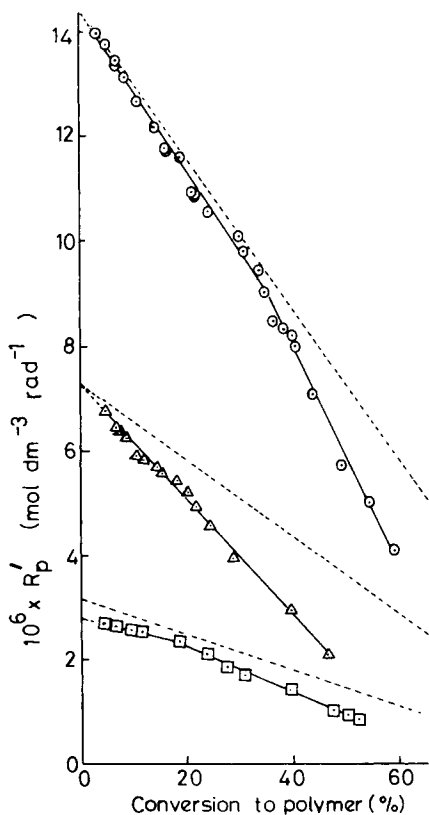


Fig. 2. Variation in the rate of polymerization to PAN with conversion to polymer for various bulk monomer/DMF compositions. Mole ratio AN:DMF: (○) 1:2; (△) 1:4; (□) 1:9.

assume an exponent and plot the data in a form such that a linear relationship is formed if that exponent applies. So, for an exponent  $x$ ,

$$R_p = \frac{-d[M]}{dt} = k[M]^x \quad (3)$$

or

$$\int \frac{d[M]}{[M]^x} = -kt \quad (4)$$

If  $x = 1$ ,

$$kt = \ln([M]/[M_0]) \quad (5a)$$

If  $x \neq 1$ ,

$$kt = \frac{1}{1-x} ([M]^{1-x} - [M_0]^{1-x}) \quad (5b)$$

Values of  $\ln([M]/[M_0])$  (for  $x = 1$ ) and  $([M]^{1-x} - [M_0]^{1-x})$  (for other values) may be plotted against the dose. If the chosen exponent is too large for the data, curved plots, concave upward, are obtained. These functions were handled as described. The initial indication is that  $x$ , the exponent, lies between 1.0 and 1.6.

Assuming initially that  $R_p$  depends on  $R_i^{1/2}$ , we have

$$R'_p = \frac{R_p}{I} = \frac{k_p[M]^x R_i^{1/2}}{(2k_t)^{1/2} I} \quad (6)$$

and, in the initial moment of homopolymerization,

$$(R'_p)_0 = \frac{k_p[M_0]^x R_i^{1/2}}{(2k_t)^{1/2} I} \quad (7)$$

$R_i$ , the rate of initiation, is the rate of formation of radicals active in initiating polymerization and  $I$  is the radiation intensity.  $k_p/(2k_t)^{1/2}$  and  $I$  can be eliminated from two pairs of  $[M_0]$  and  $(R'_p)_0$ , i.e.,

$$\frac{(R_i)_A}{(R_i)_B} = \left[ \frac{(R'_p)_{0A} \left( \frac{[M_0]_B}{[M_0]_A} \right)^x}{(R'_p)_{0B}} \right]^2 \quad (8)$$

Free radicals are produced by the action of radiation on the AN, the DMF, and the polymer when it is present. The rate of radical production can then be expressed as the sum of various factors:

$$\frac{dR\cdot}{dt} = R_i = I(\Phi_M[M] + \Phi_S[S] + \Phi_P[P]) \quad (9)$$

where  $\Phi_M$ ,  $\Phi_S$ , and  $\Phi_P$  are the rate constants for the formation of active radicals from monomer, solvent, and polymer respectively.  $[M]$ ,  $[S]$ , and  $[P]$  are the respective concentrations at any moment.

Now, two possibilities must be considered, namely, the situation which arises with the monomer and solvent only and that which applies to the monomer, solvent, and polymer being present.

### Monomer and Solvent Only

At the initial moment of polymerization, the rate of initiation,  $(R_i)_0$ , may be expressed by

$$(R_i)_0 = I\Phi_M \left( [M_0] + \frac{\Phi_s}{\Phi_M[S]} \right) \quad (9a)$$

as there is no polymer present. If a dose of  $I$  rads is absorbed per second, then  $(G_R\rho I/1.60N_A) \times 10^{15}$  mole/dm<sup>3</sup> sec of radicals are produced.  $G_R$  is the  $G$  value for radical formation,  $\rho$  is the density of the medium,  $N_A$  is the Avogadro number, and  $1 \text{ J} = 1.60 \times 10^{19} \text{ eV}$ . The rate of radical formation is then

$$R_{R\cdot} = 1.04 \times 10^{-9} G_R \rho I \text{ mole/dm}^3 \text{ sec} \quad (10)$$

If only those radicals which are effective in initiating polymerization are considered, then  $R_{R\cdot} = R_i$ , the rate of initiation. Thus, there are three separate expressions for  $R_i$ :

$$(i) R_i = 1.04 \times 10^{-9} G \rho I$$

$$(ii) R_i = I(\Phi_M[M] + \Phi_S[S] + \Phi_P[P])$$

which becomes

$$(R_i)_0 = I\Phi_M[M_0](1 + \Phi_S[S]/\Phi_M[M_0])$$

when  $[P] = 0$ .

$$(iii) R_i = [(R_p/[M]^x)^2(2k_t/k_p)] \quad (11)$$

$R_i$  can now be eliminated:

(a) between (i) and (ii)

$$G = \frac{[M_0](1 + \{\Phi_S[S]/\Phi_M[M]\}) \times 10^9 \times \Phi_M}{1.04\rho} \quad (12)$$

(b) between (i) and (iii)

$$\frac{Gk_p^2}{k_t} = \frac{(R_p/[M]^x)^2 \times 2 \times 10^9}{1.04\rho I} = \left( \frac{R'_p}{[M]^x} \right)^2 \frac{10^9 I}{0.57\rho} \quad (13)$$

(c) between (ii) and (iii).

Putting values for  $(R'_p)_0$ ,  $[M_0]$ ,  $I$ , and  $\rho$  into eq. (13) gives  $\frac{Gk_p^2}{k_t}$  as shown in

Table II.

For any value of  $x$  (as exponent in  $[M]^x$ ), a value of  $\Phi_M/\Phi_S$  can be derived from two of the three monomer concentrations. Thus,

$$(R_i)_0 = I([M_0]\Phi_M + [S]\Phi_S) \quad (9a)$$

TABLE II

x as exponent	$10^2 \times Gk_p^2/k_t$		
	$X_{AN} 0.33$	0.20	0.10
1.0	8.5	6.0	3.7
1.1	6.3	5.0	3.5
1.2	4.6	4.1	3.3
1.3	3.4	3.3	3.1
1.4	3.5	2.7	2.9

TABLE III

$x$ as exponent	$(\Phi_M/\Phi_S)_{A,B}$	$(\Phi_M/\Phi_S)_{A,C}$
1.0	9.18	9.60
1.1	4.42	4.62
1.2	2.36	2.28
1.3	0.98	0.90
1.4	0.66	0.44

$$(R_i)_{0,A} = [4.566\Phi_M + 9.132\Phi_S]I \quad (9b)$$

$$(R_i)_{0,B} = [2.684\Phi_M + 10.732\Phi_S]I \quad (9c)$$

$$(R_i)_{0,C} = [1.321\Phi_M + 11.889\Phi_S]I \quad (9d)$$

From eqs. (9b)–(9d), the values of  $\Phi_M/\Phi_S$  shown in Table III have been calculated.

$G_{\text{radical}}$  values for AN are usually quoted around 5.0. Using this value, together with  $\rho = 0.806 \text{ kg/dm}^3$  and  $[M] = 13.2 \text{ mole/dm}^3$  for pure AN in eq. (12) gives  $\Phi_M = 3.2 \times 10^{-10} (\text{mole/dm}^3)^{1/2} \text{sec}^{-1/2}$ . The  $G_{\text{radical}}$  value for 33 mole % AN, ( $[S]/[M_0] = 2.0$ ) can then be calculated from eq. (12) and  $k_p^2/k_t$  from eq. (13), as shown in Table IV.

Quoted values for  $k_p^2/k_t$  for AN in DMF are in the range of  $5.3 \times 10^{-4}$  to  $6.1 \times 10^{-3} (\text{mole/dm}^3)^{-1} \text{sec}^{-1}$ . In Table IV, only those values derived from  $x > 1.3$  are consistent with this range. Incidentally, if  $y$ , the exponent of the range in initiation, is taken to be greater than 0.5, higher values of  $k_p^{1/y}/yk_t$  are obtained. Even higher values of  $x$  would then be necessary to match these with the literature values.

### Monomer, Solvent, and Polymer

At any time after the initial moment of polymerization, the position becomes complicated by the presence of polymer. Substituting eq. (9) into eq. (2) gives

$$R_P = [k_p/(2k_t)^{1/2}][M]^x I^{1/2} (\Phi_M[M] + \Phi_S[S] + \Phi_P[P])^{1/2} \quad (14)$$

Substituting  $[P] = [M_0] - [M]$  and taking logs gives

$$\ln R_P = x \ln [M] + \frac{1}{2} \ln (1 - \Phi_P/\Phi_M)[M] + \frac{\Phi_X}{\Phi_M[S]} + \frac{\Phi_P}{\Phi_M[M_0]} + \frac{1}{2} \ln \left( \frac{k_p^2}{2k_t I \Phi_M} \right) \quad (15)$$

TABLE IV

$x$ as exponent in $[M]^x$	$G$ , events/100 eV	$10^2 \times k_p^2/k_t$ , $(\text{mole/dm}^3)^{-1} \text{sec}^{-1}$
1.0	1.86	4.56
1.1	2.22	2.82
1.2	2.87	1.61
1.3	4.81	0.71
1.4	7.12	0.35

When  $[M] = [M_0]$ ,  $R_p = (R_p)_0$ ; hence,

$$\ln \left( \frac{R_p}{(R_p)_0} \right) = x \ln \left( \frac{[M]}{[M_0]} \right) + \frac{1}{2} \ln \left\{ \frac{(1 - \Phi_P/\Phi_M)[M] + \Phi_S/\Phi_M[S] + \Phi_P/\Phi_M[M_0]}{(1 - \Phi_P/\Phi_M)[M_0] + \Phi_S/\Phi_M[S] + \Phi_P/\Phi_M[M_0]} \right\} \quad (16)$$

Thus,

$$\frac{R_p}{(R_p)_0} = \left( \frac{[M]}{[M_0]} \right)^x \left[ \frac{(1 - \Phi_P/\Phi_M)[M] + \Phi_S/\Phi_M[S] + \Phi_P/\Phi_M[M_0]}{[M_0] + \Phi_S/\Phi_M[S]} \right]^{1/2} \quad (17)$$

Rearrangement gives

$$\left[ \frac{R_p}{(R_p)_0} \right]^2 \left( \frac{[M_0]}{[M]} \right)^{2x} \left( [M_0] + \frac{\Phi_S}{\Phi_M[S]} \right) = \left( \frac{\Phi_P}{\Phi_M} - 1 \right) ([M_0] - [M]) + [M_0] + \frac{\Phi_S}{\Phi_M[S]} \quad (18)$$

Writing  $F$  for  $[R_p/(R_p)_0]^2([M_0]/[M])^{2x}([M_0] + \Phi_S/\Phi_M[S]) - [M_0] - \Phi_S/\Phi_M[S]$  yields

$$F = \left( \frac{\Phi_P}{\Phi_M} - 1 \right) ([M_0] - [M]) \quad (19)$$

A plot of  $F$  against  $([M_0] - [M])$  should have a slope of  $(\Phi_P/\Phi_M - 1)$  from which  $\Phi_P/\Phi_M$  can be derived.

For  $\chi = 1.3$  and  $1.4$  (the values giving  $k_p^2/k_t$  in agreement with literature values in the absence of polymer),  $\Phi_P/\Phi_M$  is  $0.8$  and  $2.8$ , respectively, at  $X = 0.33$ . Unfortunately, the corresponding graphs for  $X = 0.25$  and  $0.10$  give  $\Phi_P/\Phi_M$  values less than  $-1$ . This suggests that not only are radicals not produced by irradiation of the polymer in the AN/DMF/PAN system, but also that the polymer actually deactivates other radicals in this system.

The method outlined above gives reasonable values for  $\Phi_S/\Phi_M$  but presents difficulties in interpretation when used to provide values of  $\Phi_P/\Phi_M$ . One reason may be in the assumption that the total rate of radical formation is adequately expressed by the sum of the exponents  $\Phi_M[M]$ ,  $\Phi_S[S]$ , and  $\Phi_P[P]$ . This may be an oversimplification. Alternatively, the AN/DMF system may be too complex for this type of analysis. It is hoped that this approach will be applied to kinetically similar systems for which more data are available.

The authors acknowledge the support given by the International Atomic Energy Authority in this work.

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Received April 8, 1980

Accepted April 25, 1980