Bulk Polymerization of Acrylonitrile. I. An Experimental Investigation of the Kinetics of the Bulk Polymerization of Acrylonitrile

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Synopsis

A comprehensive experimental investigation is reported of the bulk polymerization of acrylonitrile (AN) to limiting conversion using 2,2'-azobisisobutyronitrile (AIBN) as initiator at 40°, 60°, and 80°C. Molecular weight development was followed by gel permeation chromatography (GPC).

INTRODUCTION

Despite numerous studies of the bulk polymerization of AN,[1-6] the kinetics of this heterophase polymerization are not well understood. This may in part be due to a lack of rate and molecular weight data over a wide range of monomer conversions and temperatures. The difficulty of modeling such a polymerization is most certainly related to the heterogeneous nature of the polymerization with polymer precipitating out of monomer at essentially zero conversion.

The purpose of this experimental investigation was to provide comprehensive rate and molecular weight data for bulk polymerization up to limiting conversions. Part II of this investigation reports on an attempt to develop a mathematical model of the bulk polymerization of AN which is capable of simulating conversion–time histories and molecular weight development for nonisothermal polymerizations up to limiting conversions using the isothermal rate and molecular weight data reported in part I.

EXPERIMENTAL

Isothermal polymerizations were done in conventional Pyrex ampoules having various surface-to-volume ratios. Ampoules having higher surface-to-volume ratios were necessary at high conversions where rates of polymerization were very high.

The initiator AIBN (Eastman Organic Chemicals) was recrystallized twice from absolute methanol before use, and the acrylonitrile monomer (AN) (practical grade, Baker Chemical Co.) was used as received without further purification.

Conversions of AN were determined by conventional gravimetry and by GPC using measurements of the areas of the AN and PAN peaks.

The molecular weight distributions (MWD) and averages ($\overline{M}_n$ and $\overline{M}_w$) were measured by GPC using a train of five columns with the following specifications.

Column no.	Packing Material	Pore size, Å
1	deactivated Porasil	2500
2	deactivated Porasil	1500/800
3	deactivated Porasil	800/200
4	Styragel	2000/700
5	Styragel	100/20

The carrier solvent was DMF containing $0.05M$ lithium bromide with a flow rate of 2.5 ml/min at room temperature.

Two methods were used to calibrate the GPC. These included the determination of an effective linear molecular weight calibration curve and the use of the universal molecular weight calibration curve.

Effective Linear Molecular Weight Calibration Curve

The effective linear molecular weight calibration curve was obtained using a single broad MWD copolymer standard provided by A. S. Kenyon (Monsanto Co., St. Louis, Missouri).[7,8] This standard contains 94% AN and 6% styrene and was characterized at Monsanto Co. using osmometry and viscometry. The molecular weights provided are $\overline{M}_n = 38,800$ and $\overline{M}_w = 117,000$. The use of this SAN standard for PAN polymers of course implies the assumption that the presence of 6% styrene in the SAN molecules does not significantly affect the relationship between molecular size and weight in DMF/LiBr solutions. The equation for the effective linear molecular weight calibration curve obtained is $M(V) = 3.545 \times 10^9 \exp(-0.3315V)$, where V is the retention volume in counts.
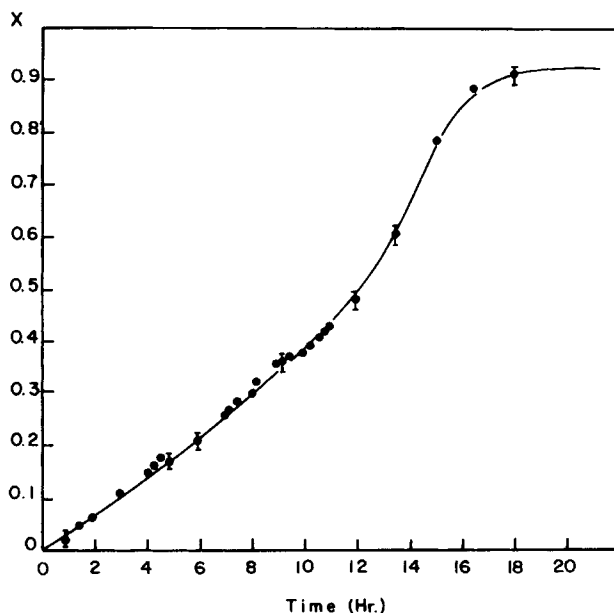

Fig. 1. Conversion–time history for bulk polymerization of acrylonitrile at 60°C with AIBN initiator at 0.025 wt-% showing individual 95% C.I. for replicates.
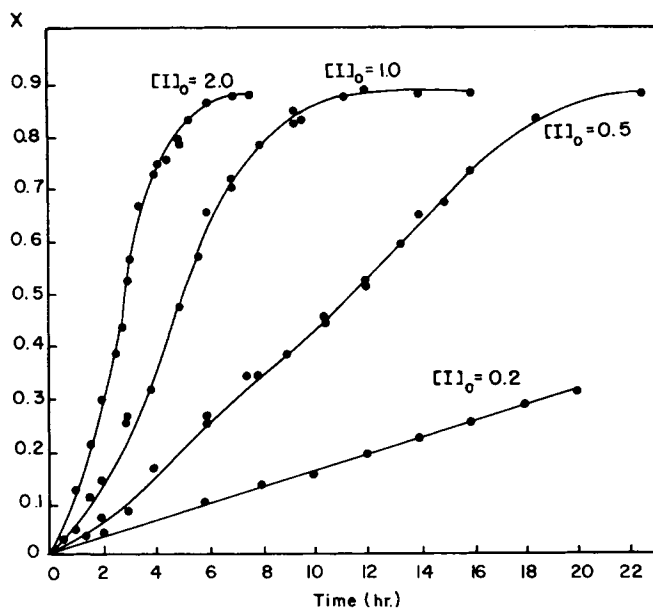
Fig. 2. Conversion–time histories for bulk polymerization of acrylonitrile at 40°C at various AIBN levels.
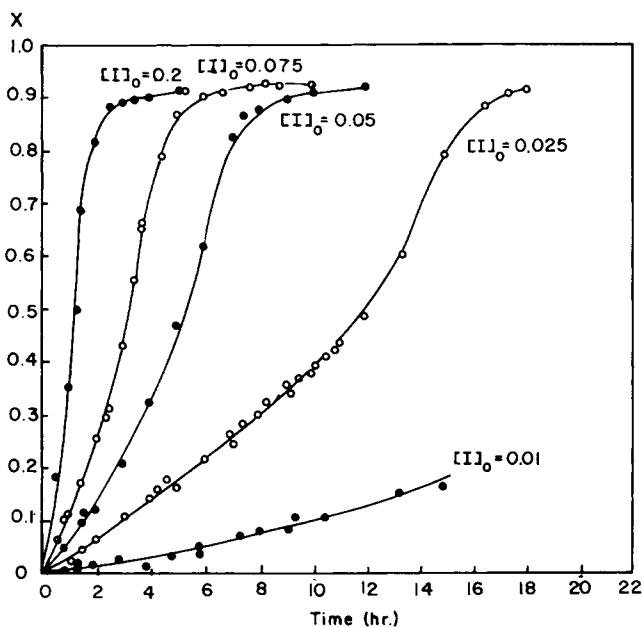

Fig. 3. Conversion–time histories for bulk polymerization of acrylonitrile at 60°C at various AIBN levels.

Universal Molecular Weight Calibration Curve

Constants in the Mark–Houwink equation were measured for monodisperse polystyrene standards in $0.05M$ LiBr/DMF at 25°C to give $[\eta] = 5.893 \times 10^{-4}M^{0.549}$ for the molecular weight range of 2×10^4–1.8×10^6. The units of intrinsic viscosity are deciliters per gram (dl/g).
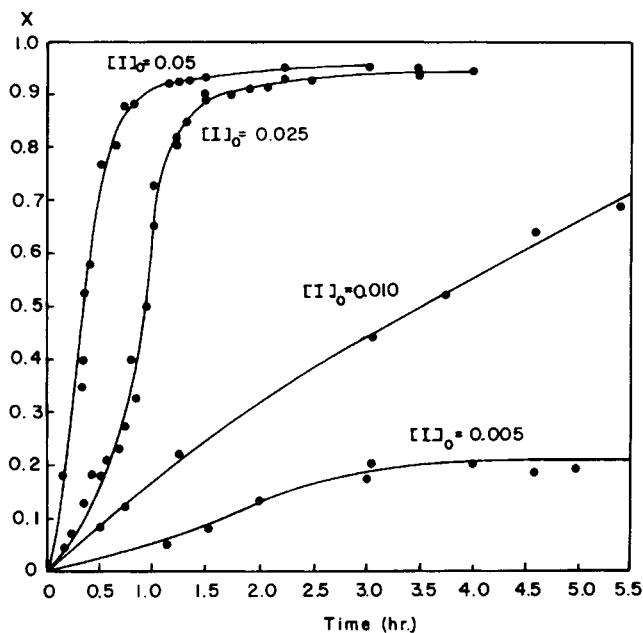
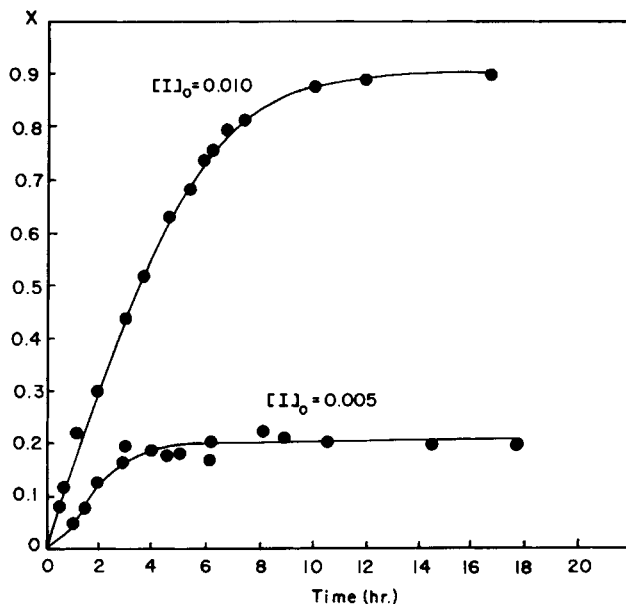Fig. 4. Conversion–time histories for bulk polymerization of acrylonitrile at 80°C at various AIBN levels.

Fig. 5. Conversion–time histories for bulk polymerization of acrylonitrile at 80°C at various AIBN levels.

Two sets of Mark–Houwink constants were determined for PAN—effective and true. Here again the Monsanto SAN standard was employed. Effective Mark–Houwink constants were obtained with a single-variable search using the following equations:
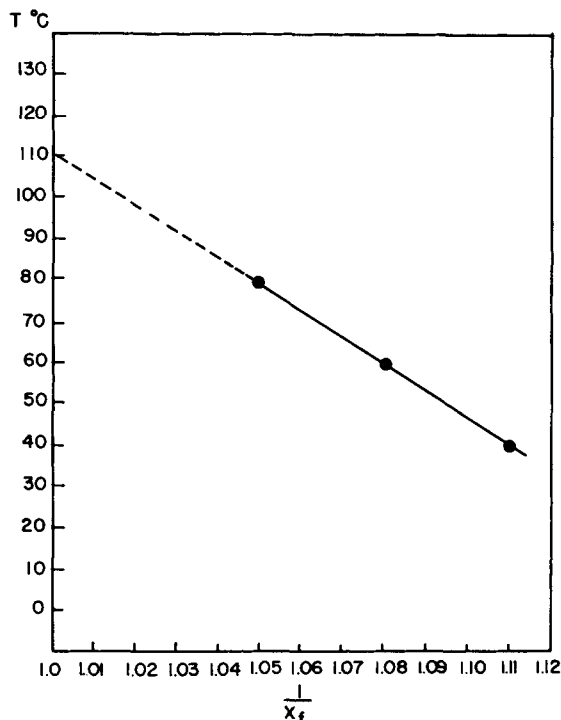
$$[\eta](V)M(V) = f(V) \tag{1}$$

T °C

Fig. 6. Variation of limiting conversion with polymerization temperature in presence of excess initiator for bulk polymerization of acrylonitrile.

which is the universal weight calibration curve based on polystyrene;

$$[\eta](V) = \overline{K}M(V)^{\overline{a}} \tag{2}$$

where $\overline{K}$ and $\overline{a}$ are the Mark–Houwink constants for PAN in 0.05M LiBr/DMF at 25°C; and

$$\overline{M}_w(t) = 117,000 = \frac{1}{\overline{K}^\alpha} \int_0^\infty F(V)f(V)^\alpha \, dV \tag{3}$$

$$\frac{\overline{M}_w(t)}{\overline{M}_n(t)} = 3.02 = \left\{ \int_0^\infty F(V)f(V)^\alpha \, dV \right\} \left\{ \int_0^\infty F(V)f(V)^{-\alpha} \, dV \right\} \tag{4}$$

where $\alpha = (1/1 + \overline{a})$. It was found that $\overline{K} = 4.284 \times 10^{-3}$ and $\overline{a} = 0.516$.

There are several procedures one can follow to determine true Mark–Houwink constants for PAN in 0.05M LiBr/DMF. These are all based on the concept that the resolution factor h which corrects for uniform Gaussian axial dispersion depends only upon molecular size in solution. An h-versus-retention volume relationship determined for polystyrene should therefore be applicable to other polymers and in this particular instance to PAN. We therefore measured h versus retention volume for narrow MWD polystyrene standards using eqs. (5) and (6):

$$\overline{M}_n(t) = \overline{M}_n(\infty) \exp(D_2^2/4h) \tag{5}$$

$$\overline{M}_w(t) = \overline{M}_w(\infty) \exp(-D_2^2/4h) \tag{6}$$

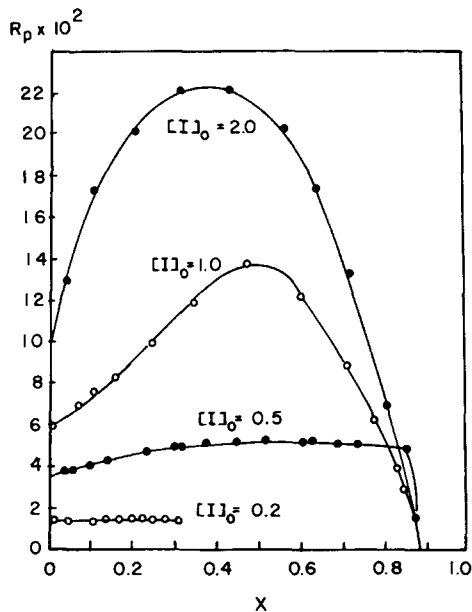From this point on there are two obvious routes to follow to obtain true

Fig. 7. Rate of polymerization vs. conversion for bulk polymerization of acrylonitrile at 40°C and at various AIBN levels.
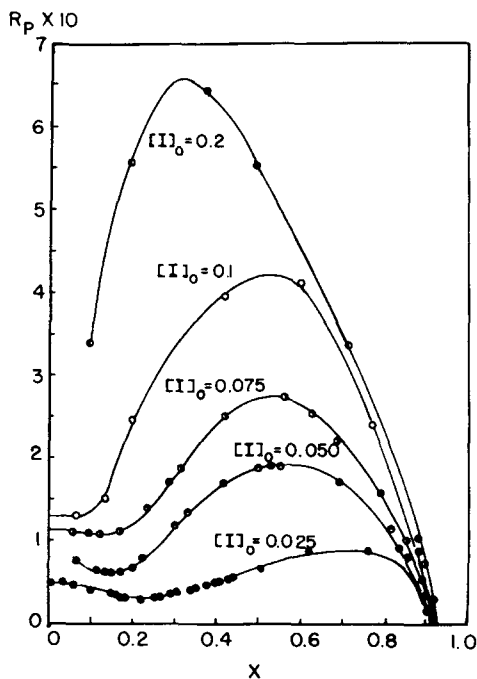

Fig. 8. Rate of polymerization vs. conversion for bulk polymerization of acrylonitrile at 60°C and at various AIBN levels.

Mark–Mouwink constants for PAN. One is to correct the PAN chromatogram using the appropriate resolution factor h and solving Tung's integral equation with a uniform Gaussian instrumental spreading function. This corrected
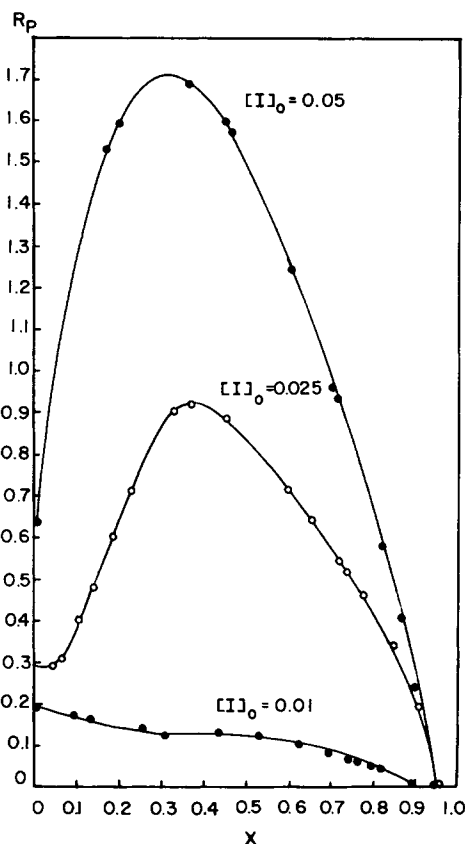
Fig. 9. Rate of polymerization vs. conversion for bulk polymerization of acrylonitrile at 80°C and at various AIBN levels.

chromatogram $w(V)$ is then used in place of the uncorrected chromatogram $F(V)$ in eqs. (3) and (4). A solution of eqs. (3) and (4) would then give true Mark–Houwink constants for PAN. The second route involves the replacement of $\overline{M}_n(t)$ and $\overline{M}_w(t)$ by $\overline{M}_n(\infty)$ and $\overline{M}_w(\infty)$ in eqs. (3) and (4). These latter averages can be determined using eqs. (5) and (6) with D_2 being the slope of the true molecular weight calibration curve for PAN at the peak position for the broad MWD SAN standard. We chose the second route and obtained the true Mark–Houwink constants for PAN in 0.05M LiBr/DMF at 25°C to be $K = 1.297 \times 10^{-3}$ and $a = 0.636$. In conclusion, it may be reported that all the above methods give essentially the same $\overline{M}_n$ and $\overline{M}_w$ for polymers that fall within the universal calibration curve range. For polymers that are close to the upper limit of the universal calibration curve, the effective linear calibration gives more conservative estimates of the molecular weights.

For purposes of kinetic modeling it was necessary to measure the solubility of AN in PAN at polymerization temperatures. The solubility was measured gravimetrically by following the absorption of AN into a cylindrical rod of PAN as a function of time in the temperature range of 0°–80°C. The solubility of AN in PAN was found to be about 10 wt-% in this temperature range.
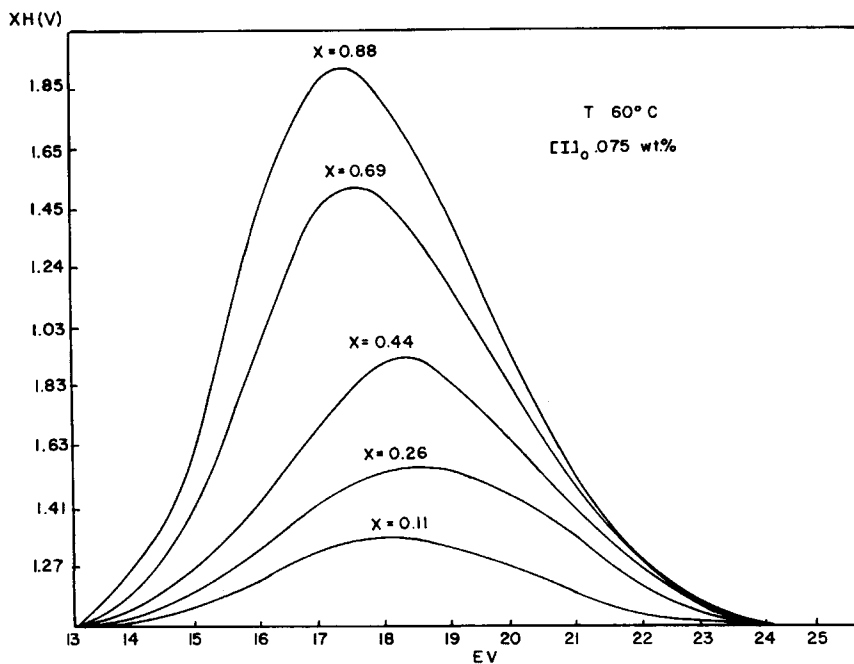
Fig. 10. GPC chromatograms showing molecular weight development for bulk polymerization of acrylonitrile at 60°C and at a single AIBN level.
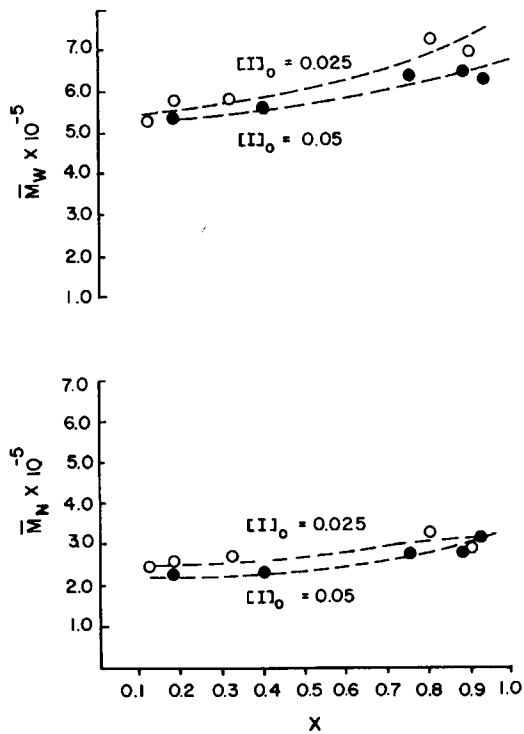

Fig. 11. Molecular weight development for bulk polymerization of acrylonitrile at 80°C and at various AIBN levels.
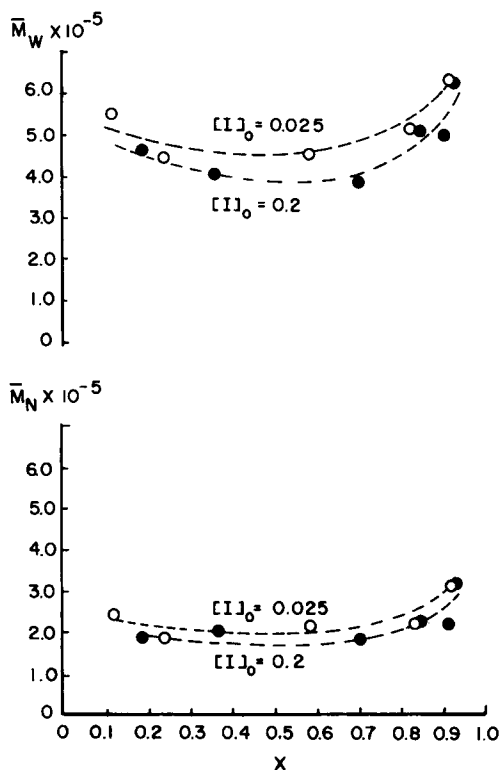
Fig. 12. Molecular weight development for bulk polymerization of acrylonitrile at 60°C and at various AIBN levels.

Polymerization conditions studied in this investigation are given in Table I.

Investigations of reproducibility of conversion and molecular weight averages ($\overline{M}_n$ and $\overline{M}_w$) were made. The 95% confidence intervals for a single determination were estimated to be $\overline{M}_n \pm 0.128 \times 10^5$, $\overline{M}_w \pm 0.25 \times 10^4$, and $X \pm 0.008$. All molecular weight averages and conversions shown in the figures are averages of two to seven determinations. Individual confidence intervals for some of these averages are shown in Figure 1.

Details of all experimental measurements may be found elsewhere.[9]

TABLE I
Isothermal Bulk Polymerization of Acrylonitrile. Reaction Conditions Investigated

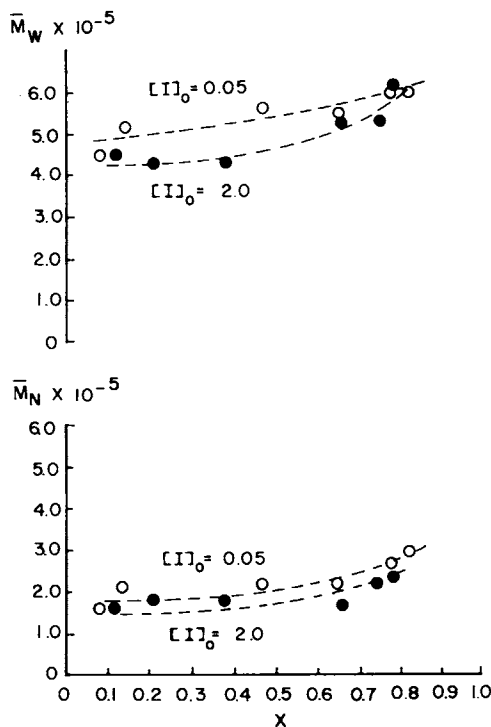| Temperature, °C	Initiator concentration, wt-% AIBN
0	2.0
25	2.0
40	0.2–2.0
50	0.1
60	0.01–0.2
70	0.1
80	0.005–0.05
100	0.1
120	0.1

Fig. 13. Molecular weight development for bulk polymerization of acrylonitrile at 40°C and at various AIBN levels.

RESULTS AND DISCUSSION

Conversion–Time Histories

Figures 1–5 illustrate conversion–time histories for temperature levels of 40°, 60°, and 80°C at a number of initiator concentrations. At the higher initiator concentrations the conversion–time curves have the characteristic sigmoidal shape showing the acceleration in rate of polymerization with conversion and then an abrupt fall to zero rate at a limiting conversion less than 100%. These features are observed in both homogeneous (methyl methacrylate[10]) and heterogeneous (vinyl chloride[11]) bulk free-radical polymerization. In both homogeneous and heterogeneous polymerization the acceleration in rate is a consequence of diffusion-controlled termination reactions, and the limiting conversion is reached when the polymer–monomer solution becomes a glass.[12] The situation is more complex when the polymer precipitates from its monomer giving two loci of polymerization: the essentially polymer-free monomer phase and a polymer phase that contains dissolved monomer. The polymer phase may be saturated with monomer or there may exist monomer concentration gradients within the precipitated polymer particles. Diffusion-controlled termination reactions are found in the polymer phase giving a higher specific polymerization rate in this growing locus of reaction. At lower initiator concentrations the acceleration in rate of polymerization is not so apparent, and in some instances at the higher temperatures (see Fig. 5) a limiting conversion is reached due to consumption
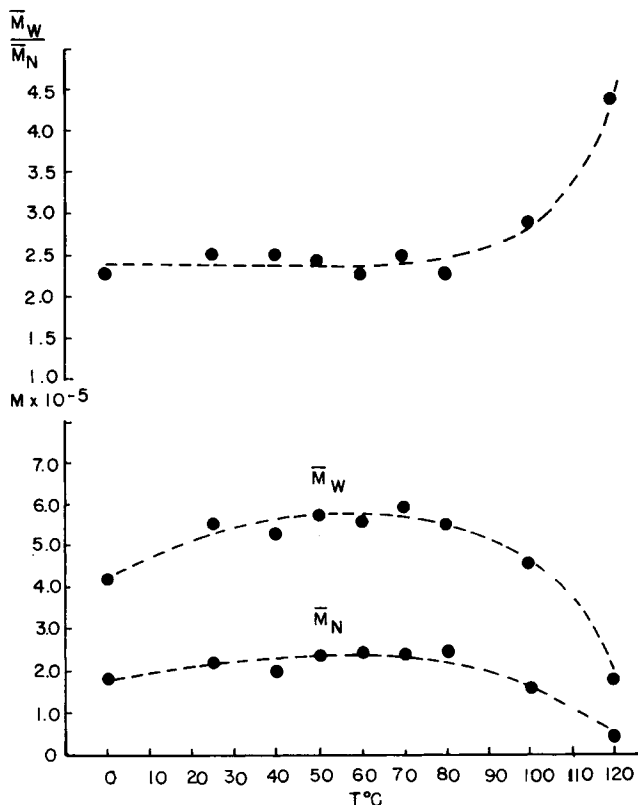
Fig. 14. Molecular weight development for bulk polymerization of acrylonitrile at various temperature levels.

of initiator. Limiting conversions (X_f) measured under conditions where excess initiator was present are shown plotted in Fig. 6. Extrapolation to a limiting conversion of 100% gives an estimate of the glass transition point T_g for PAN of about 110°C, which is in reasonable agreement with T_g values quoted in the literature and measured by standard techniques such as DSC.[13-15] In kinetic modeling it is of interest to observe the variation of rate of polymerization with conversion. Spline functions[16] were used to fit the conversion–time data, which were then differentiated. Third-order splines gave adequate fits, with the least-squares error being less than 2% for almost all the data. Figures 7–9 illustrate the variation of polymerization rate R_p with conversion at different temperature and initiator levels. The following important conclusions can be drawn from an observation of these rate curves: (i) The duration of the autoacceleration period depends strongly upon temperature and initiator concentration. (ii) The value and position of the maximum polymerization rate depend strongly upon temperature and initiator concentration. (iii) Limiting conversion (X_f) with excess initiator is a function of temperature and effectively independent of initiator concentration.

With the bulk polymerization of AN, the maximum polymerization rate occurs at low conversions, where both monomer and polymer phases are present in appreciable amounts. This observation is in contrast with that observed with
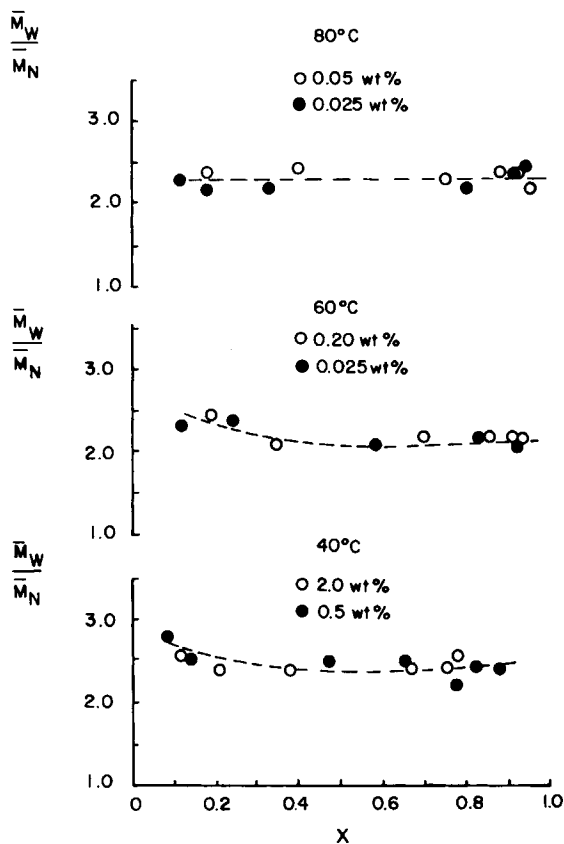
Fig. 15. Polydispersity variation temperature, conversion, and AIBN level for bulk polymerization of acrylonitrile.

the bulk polymerization of vinyl chloride, where the maximum polymerization rate occurs after the monomer phase has been consumed, which is due to a competition between diffusion-controlled termination and diffusion-controlled propagation.   In vinyl chloride bulk polymerization, it is assumed that the polymer phase is saturated with monomer during the entire life of the monomer phase.   The consequence of polymer phase saturation is that the rate of polymerization should continue to increase as the volume of the polymer phase is growing at the expense of the monomer phase.   In the bulk polymerization of AN, a comparable situation of saturation of polymer phase by monomer would result in a maximum polymerization rate occurring near 90% conversion (the monomer phase is consumed at about 90% conversion).   The rate data for AN, therefore, strongly suggest that the polymer phase is not homogeneous and that monomer concentration gradients exist in the precipitated polymer particles. This could lead to a premature limiting conversion in the center of the polymer particles and a glassy nonreacting core.   It is obvious from even this preliminary interpretation of the AN bulk polymerization that the simple two-phase model proposed for the bulk polymerization of vinyl chloride[11] would not be valid in this more complex system.

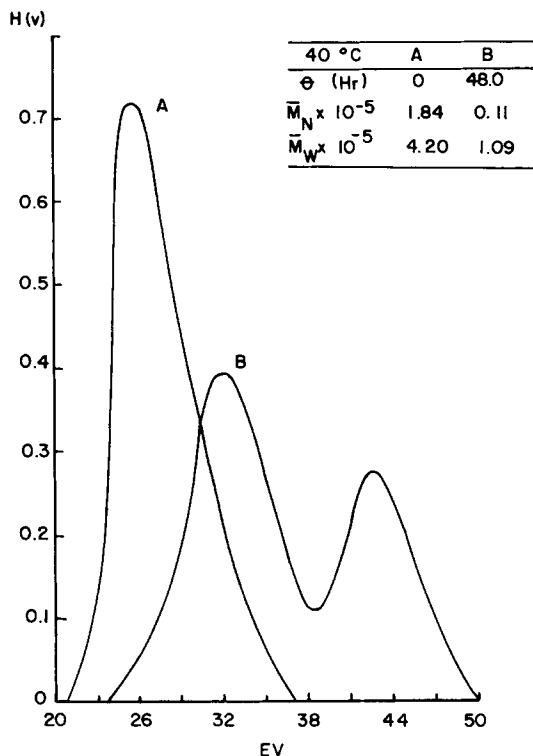| 40 °C	A	B
θ (Hr)	0	48.0
$\overline{M}_N \times 10^{-5}$	1.84	0.11
$\overline{M}_W \times 10^{-5}$	4.20	1.09

Fig. A-1. GPC response for polyacrylonitrile thermal degradation at 120°C (polymer produced at 40°C).

Molecular Weight Development

Figure 10 illustrates typical GPC chromatograms obtained at different conversions of AN. The raw chromatograms were first normalized and the ordinate multiplied by the conversion X. As plotted in Figure 10, the area under the chromatogram is proportional to the amount of polymer produced. With this graph form one is able to examine how the synthesis of various molecular weights changes with conversion (smaller elution volumes EV represent larger molecular weights). The molecular weight distribution is almost independent of conversion for conversions up to 44%. At higher conversions, however, there is a clear shift to the production of higher molecular weight species. The shift appears to occur near the point where the maximum in polymerization rate is observed (see Fig. 8). There are insufficient data near the point of maximum rate to permit anything more than speculation about this correspondence. However, under all polymerization conditions investigated the molecular weight averages ($\overline{M}_n$ and $\overline{M}_w$) increased with conversion (Figs. 11–13). Some preliminary syntheses of PAN at 100° and 120°C and molecular weight measurements by GPC indicated a rapid falloff in molecular weight at these elevated temperatures. This rapid falloff in molecular weight includes two effects: the expected drop in molecular weight due to the change in rate constants with temperature and some extent of thermal degradation depending on the particular polymerization temperature[17,18] (see also Appendix). The effect of temperature on molecular weight

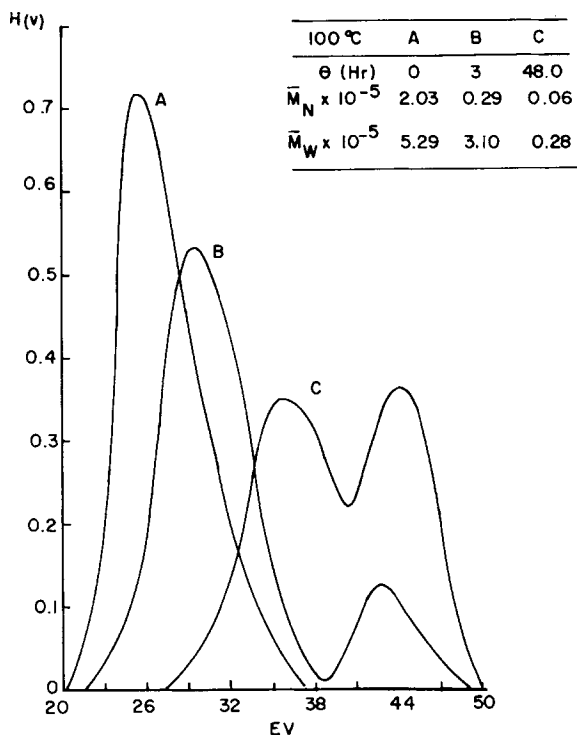| 100 °C	A	B	C
θ (Hr)	0	3	48.0
$\bar{M}_N \times 10^{-5}$	2.03	0.29	0.06
$\bar{M}_W \times 10^{-5}$	5.29	3.10	0.28

Fig. A-2. GPC response for polyacrylonitrile thermal degradation at 120°C (polymer produced at 100°C).

averages and polydispersity is summarized in Figure 14. The effect of conversion and initiator level on molecular weight was small, and it was therefore desirable to eliminate these as parameters in Figure 14 by using averaged molecular weight values to clearly show the effect of temperature. The gradual increase in molecular weight averages with temperature in the range of 0°–80°C was surprising, as one normally expects a fall with temperature increase. The variation of polydispersity with temperature, initiator level, and conversion is summarized in Figure 15. Polydispersity is likely constant with these reaction variables within experimental error.

The further quantitative interpretation of the conversion–time histories and molecular weight development for the bulk polymerization of AN is left to part II of this investigation.

Appendix

To establish whether degradation of PAN was occurring at temperatures above 80°C, solutions containing polymer produced at three different temperatures were heated in the presence of oxygen at 120°C for several periods of time. The solutions were quenched and injected into the GPC at room temperature. The chromatograms (Figs. A-1 to A-3) show a continuous growth of the low molecular weight tail and therefore a systematic decrease in molecular weight with increasing heating time. Based on these experimental observations, the following conclusions were drawn:

(1) Polyacrylonitrile degrades thermally at relatively low temperatures.

(2) Polymers produced at high temperatures degrade more rapidly than those produced at lower temperatures.

(3) Thermal degradation of PAN is very slow at temperatures below 80°C. Therefore, for most
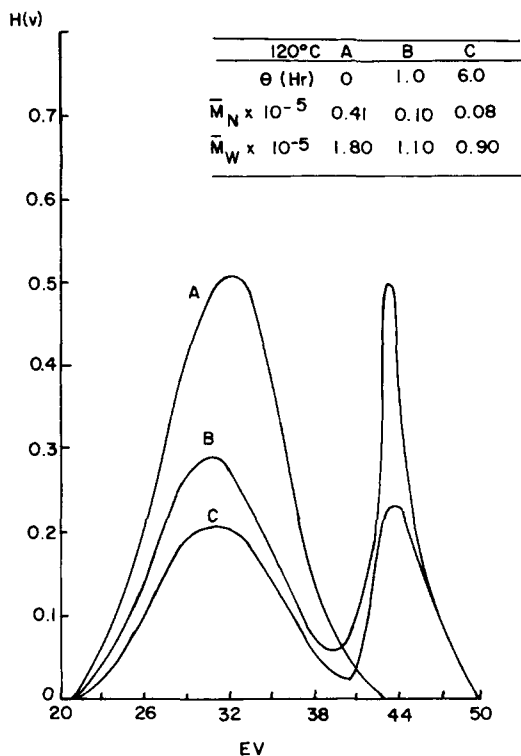
Fig. A-3. GPC response for polyacrylonitrile thermal degradation (polymer produced at 120°C).

reactor calculations where the polymerization temperature is below 80°C, molecular weight calculations need not consider thermal degradation of PAN.

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