

# Estimation of Transfer Constants in the Aqueous Solution Polymerization of Acrylamide with Potassium Persulfate Initiator

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## Synopsis

An experimental investigation on the aqueous polymerization of acrylamide with potassium persulfate initiator is reported. Molecular weight averages were measured by viscometry. Non-Newtonian effects were accounted for by extrapolation to high shear rates where the polymer solutions approximated Newtonian behavior. Values for the transfer constants to the acrylamide monomer and to the persulfate initiator were estimated at 25 and 40°C and compared to literature values.

## INTRODUCTION

Kinetic studies of the polymerization of acrylamide have been carried out using a number of different initiator systems. The termination reaction has been proven to be mainly through disproportionation.<sup>1</sup> Water as a solvent has been shown to have a chain transfer constant of practically zero.<sup>2</sup> Transfer to polymer was shown to be negligible at reaction temperatures of 50°C or less.<sup>3</sup> Therefore, assuming no chain transfer agent is used, the free radical chain polymerization model predicts<sup>4</sup>

$$\frac{1}{\bar{r}_n} = \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p} \frac{[I]}{[M]} \quad (1)$$

where  $\bar{r}_n$  is the instantaneous number-average chain length of the resulting polymers;  $[I]$  and  $[M]$  are the instantaneous concentrations of initiator and monomer, respectively;  $R_p$  is the instantaneous rate of polymerization;  $k_p$  is the propagation rate constant;  $k_t$  is the termination rate constant;  $k_{fm}$  is the transfer-to-monomer rate constant; and  $k_{fi}$  is the transfer to initiator rate constant.

The following expression was found to describe the variation of  $k_p/k_t^{1/2}$  with temperature, in the units of (l/mol-sec)<sup>1/2</sup> with  $T$  in K.<sup>5</sup>

$$k_p/k_t^{1/2} = 57 \exp(-1500/2T) \quad (2)$$

Furthermore, the above ratio was found to remain almost constant over a pH range of 1 to 13.<sup>6</sup> The rate expression for the polymerization of acrylamide in water with potassium persulfate ( $K_2S_2O_8$ ) initiator was found by Riggs and Rodriguez<sup>7</sup> to be

$$R_p = k_{1.25}[I]^{0.50}[M]^{1.25} \quad (3)$$

with the empirical rate constant  $k_{1.25}$  conforming to the Arrhenius expression

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$$k_{1.25} = 1.70 \times 10^{11} \exp(-16,900/1.99 T) \quad (4)$$

where  $T$  is in K and  $k_{1.25}$  in  $l^{0.75}/mol^{0.75}\cdot min$ . The cage effect theory was favored by the authors to explain the order with respect to  $[M]$  in eq. (3).

The value of the ratio  $k_{fm}/k_p$  associated with the transfer reaction to the monomer molecules has not been as unequivocally defined. Table I summarizes the values reported in the literature for this ratio.

It is clear from Table I that the values reported for  $k_{fm}/k_p$  at 25°C vary by a factor of 20; and at the higher temperature level of 40–60°C, the values vary by a factor of 10. This latter variation cannot be explained by the difference in temperature from one investigator to the other. These uncertainties in the value of  $k_{fm}/k_p$  would cause differences of several orders of magnitude in the molecular weights of the resulting polymers, especially since Ishige and Hamielec have shown that transfer to monomer plays a dominant role in controlling the molecular weight averages.<sup>13</sup>

All the above studies used viscometry to determine the average molecular weights of the polymers produced. No provisions were taken to correct for non-Newtonian effects when estimating the intrinsic viscosities of polyacrylamides having molecular weight averages of several million. We have shown in our previous publication that this practice may introduce a considerable error in the computed molecular weights, rendering the values of  $k_{fm}/k_p$  based upon them doubtful. No estimate of the transfer constant  $k_{fi}/k_p$  to the initiator  $K_2S_2O_8$  is available in the literature.

Hence, the present experimental investigation was undertaken to estimate the values of  $k_{fm}/k_p$  and  $k_{fi}/k_p$  for acrylamide- $K_2S_2O_8$  polymerization. Molecular weight averages were to be calculated from viscosity data that have been corrected for shear rate effects.

### EXPERIMENTAL DETAILS

Acrylamide, supplied by Eastman Kodak Co., Rochester, New York, was twice recrystallized from chloroform. The water used as polymerization medium and for viscosity measurements was doubly distilled, the second distillation being from alkaline potassium permanganate. The potassium persulfate initiator was purchased from Fisher Scientific Co., Fair Lawn, New Jersey. It was recrystallized twice from twice-distilled water at 60°C.

It has been observed that freeze and thaw techniques commonly used for deaerating reaction ampoules in polymer chemistry were difficult to use in

TABLE I  
Transfer Constant to Acrylamide Monomer

$k_{fm}/k_p$	Temp., °C	Reference
$<10^{-6}$	25	Collinson, Dainton, and McNaughton <sup>5</sup>
$1.2 \times 10^{-5}$	25	Dainton and Tordoff <sup>6</sup>
$1.6 \times 10^{-5}$	25	Cavell <sup>9</sup>
$2.0 \times 10^{-5}$	25	Cavell and Gilson <sup>10</sup>
$2.0 \times 10^{-5}$	25	Fadner and Morawetz <sup>11</sup>
$5.8 \times 10^{-4}$	40	Kwangfu <sup>12</sup>
$1.45 \times 10^{-5}$	50	Ishige <sup>13</sup>
$6.0 \times 10^{-5}$	60	Fadner and Morawetz <sup>11</sup>

conjunction with the polymerization of acrylamide since considerable amount of polymerization occurred during the thawing steps.<sup>5</sup> To circumvent this difficulty in the present study, deaeration of separate solutions of the monomer and initiator was effected in the apparatus shown in Figure 1. It consists of a vacuum line, a nitrogen line, and two ice-jacketed 50-ml burets (A and B in the figure) containing the monomer and the initiator solutions, respectively. First, the air in the tubes of the apparatus was replaced by nitrogen through five alternate steps of application of vacuum and refilling with nitrogen. Then nitrogen was bubbled through the solutions for 1 hr. A reaction ampoule was then connected to the bottom of the deaeration apparatus, and the air inside the ampoule was replaced by nitrogen, as before. Then the required volumes of the monomer and initiator solutions were introduced into the ampoule that was kept in an ice bath. The ampoule was then sealed and the reaction started by transferring the ampoule into a thermostated bath.

The reaction ampoules were made of Pyrex glass and had the following dimensions: O.D. = 12 mm, I.D. = 10 mm, and length = 300 mm. Ampoules of this size have been proved to provide isothermal conditions during the polymerization of acrylamide at rates comparable to the ones encountered in the present study.<sup>13</sup>

Each reaction was quenched at the desired time by thrusting the corresponding ampoule in liquid nitrogen. The ampoule was then broken and its contents added to about ten times its volume of distilled water to which hydroquinone inhibitor had been added. When dilution was complete, the polymer was precipitated out by adding the mixture dropwise to more than ten times its volume of methanol that was being stirred vigorously by a magnetic stirrer. The polymers were filtered out, washed with benzene, and dried to constant weight at 40°C under vacuum. Conversion was thus determined gravimetrically.

The number-average molecular weights of the polymers were calculated from their intrinsic viscosities extrapolated to high shear rates  $[\eta]_{\infty}$ ; where the polymer solutions approached Newtonian behavior. The empirical relation used for this calculation was

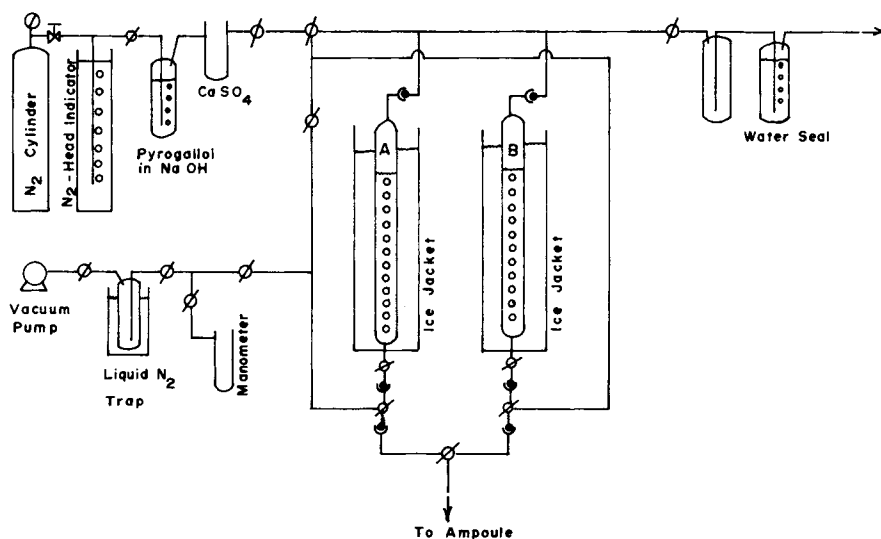


Fig. 1. Schematic diagram of deaeration apparatus.

$$[\eta]_{\infty} = 6.80 \times 10^{-4} \bar{M}_n^{0.66} \quad (5)$$

The description of the four-bulb viscometer used for the viscosity measurements, as well as the reason for using  $[\eta]_{\infty}$  in conjunction with eq. (5), were detailed in our previous publication.

The experimental conditions of all the polymerization runs are summarized in Table II.

## RESULTS AND DISCUSSIONS

Figures 2 to 13 represent the experimental results from all the polymerization runs conducted. The points that are "filled in" represent polymers produced

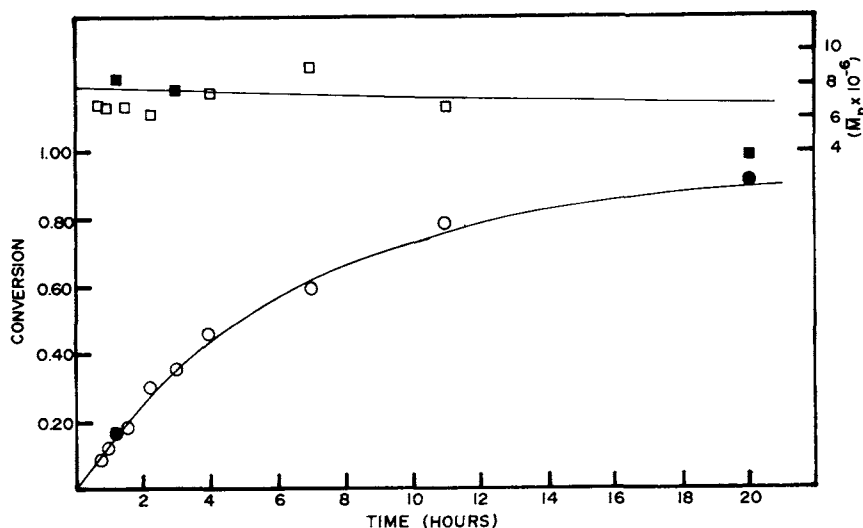


Fig. 2. Run (25-20-10).

TABLE II  
Summary of Experimental Conditions

Run No.	Temp., °C	Initial monomer concentration, g · mol/l	Initial initiator concentration, g · mol/l
25-20-10	25	2.00	$10^{-3}$
25-05-10	25	0.50	$10^{-3}$
25-02-10	25	0.20	$10^{-3}$
25-05-01	25	0.50	$10^{-4}$
25-05-05	25	0.50	$5.0 \times 10^{-4}$
25-05-25	25	0.50	$2.5 \times 10^{-3}$
40-20-05	40	2.00	$5.0 \times 10^{-4}$
40-05-05	40	0.50	$5.0 \times 10^{-4}$
40-02-05	40	2.00	$5.0 \times 10^{-4}$
40-05-01	40	0.50	$10^{-4}$
40-05-15	40	0.50	$1.5 \times 10^{-3}$
40-05-25	40	0.50	$2.5 \times 10^{-3}$

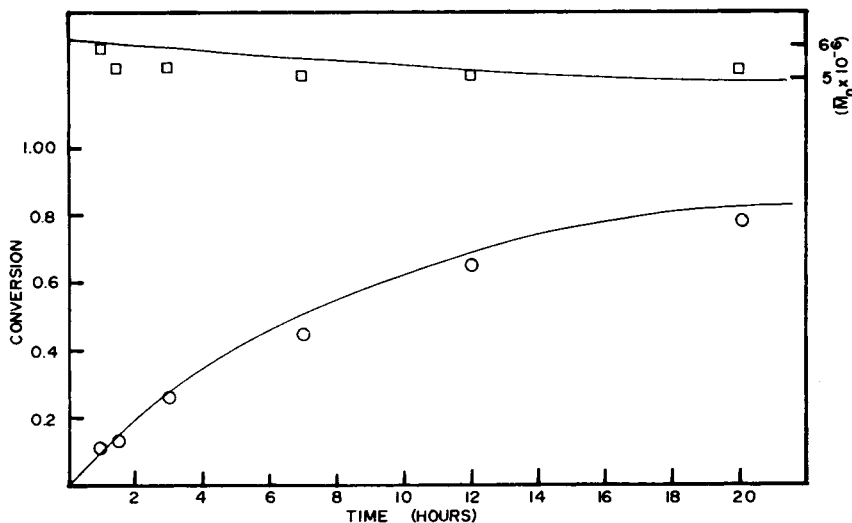


Fig. 3. Run (25-05-10).

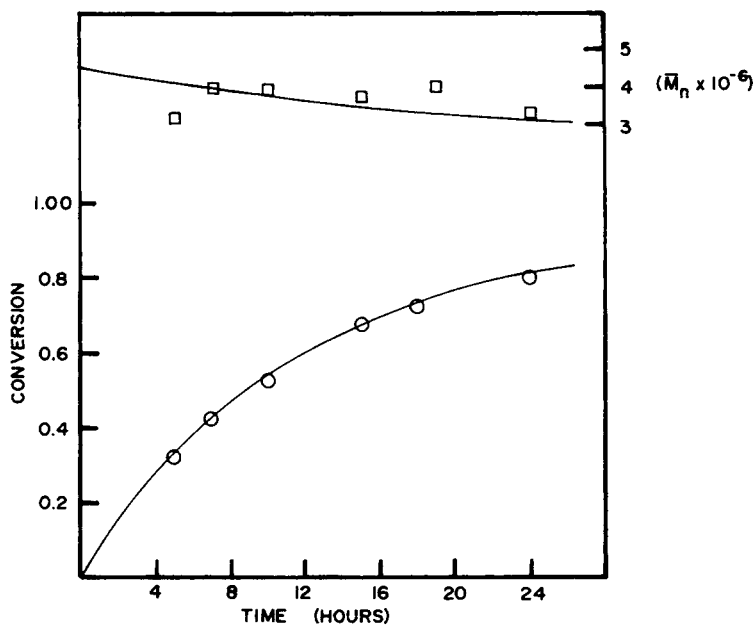


Fig. 4. Run (25-02-10).

in a duplicate run where all the experimental conditions were identical to the original run. This was done to ascertain the reproducibility of the conversion and molecular weight measurements. In each figure the lower curve is the conversion-time relationship, whereas the upper curve is the variation of  $\bar{M}_n$  with time (hence conversion).

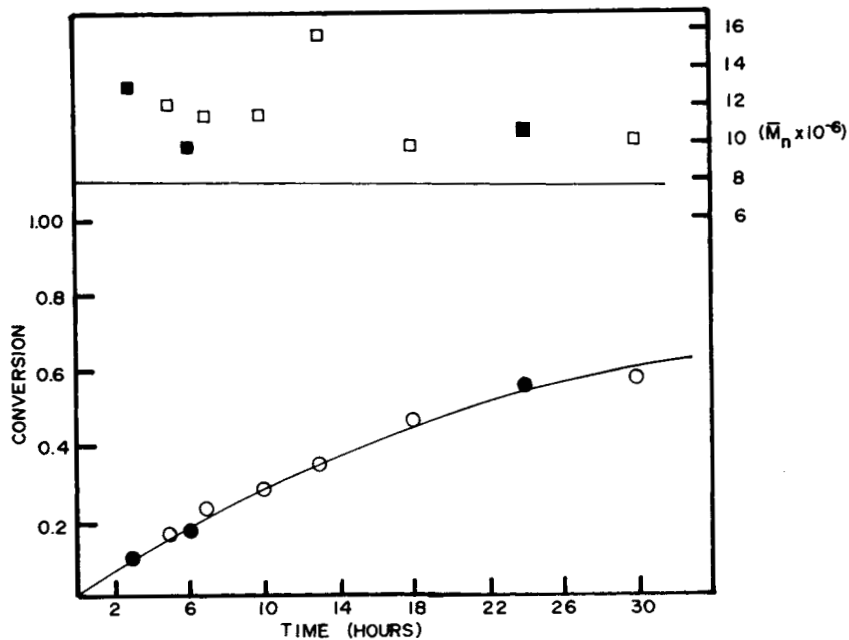


Fig. 5. Run (25-05-01).

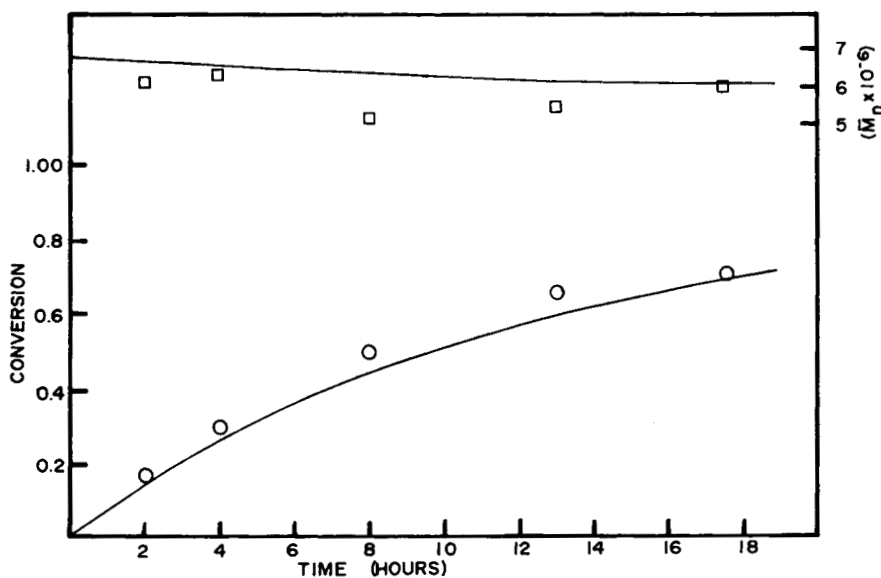


Fig. 6. Run (25-05-05).

### Decomposition of the Potassium Persulfate Initiator

The kinetics of thermal decomposition of  $K_2S_2O_8$  in aqueous solutions have been investigated by Kolthoff and Miller.<sup>14</sup> They found that, except in strongly acidic solutions,  $K_2S_2O_8$  decomposed through a first-order reaction. From their results the values of the dissociation constant at 25 and 40°C were calculated

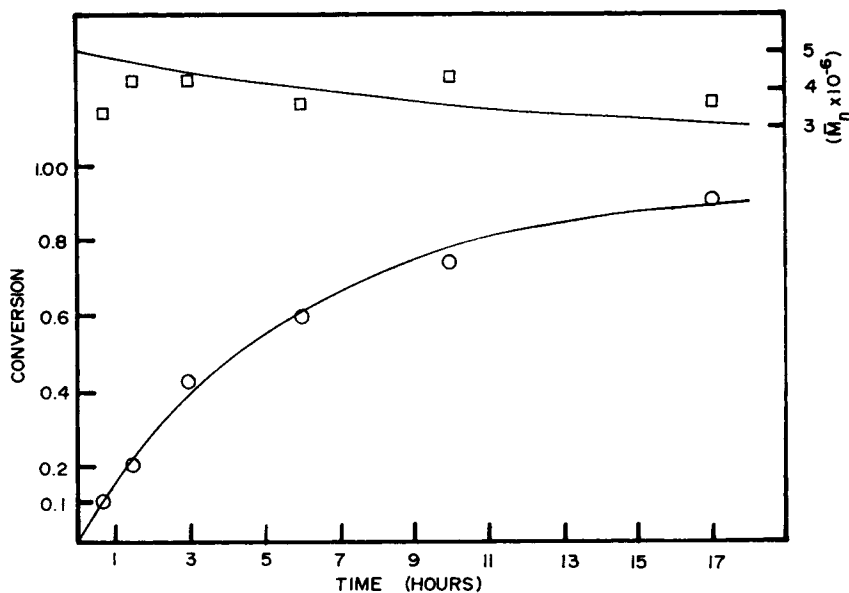


Fig. 7. Run (25-05-25).

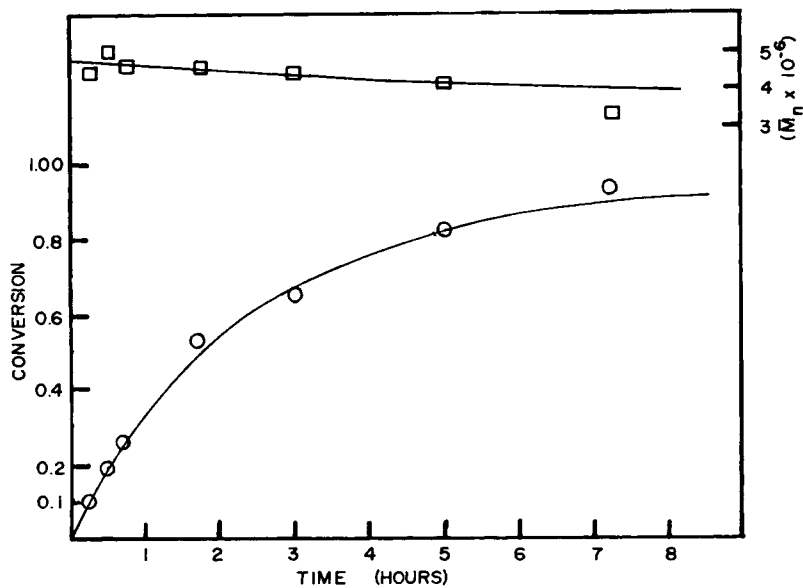


Fig. 8. Run (40-20-05).

as  $7.7 \times 10^{-7}$  and  $1.1 \times 10^{-5} \text{ (min)}^{-1}$ , respectively. Hence, the time necessary for the concentration of  $\text{K}_2\text{S}_2\text{O}_8$  to decrease by 2% of its original value at these temperatures was estimated to be 440 and 31 hr, respectively. As all polymerization reactions were terminated in a time less than that, it is reasonable to assume that the concentration of  $\text{K}_2\text{S}_2\text{O}_8$  remained virtually constant throughout the polymerization reactions. Therefore,  $[\text{I}]$  in eqs. (1) and (3) may be replaced

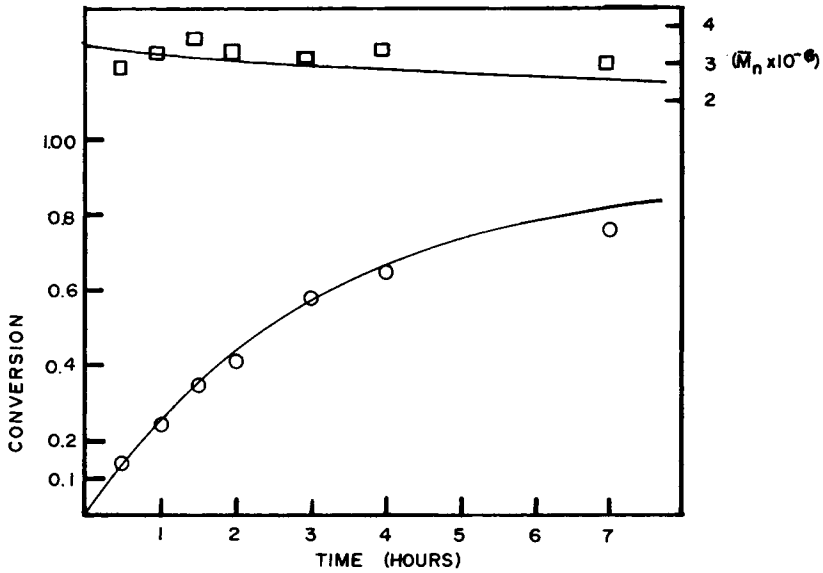


Fig. 9. Run (40-05-05).

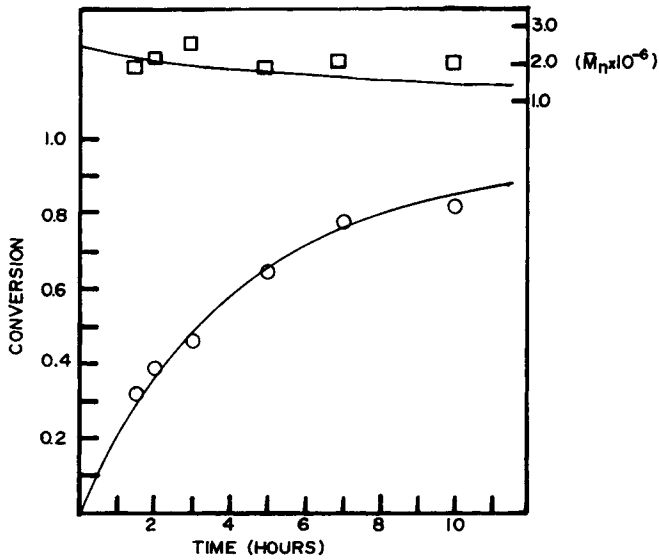


Fig. 10. Run (40-02-05).

by  $[I_0]$ , the original concentration of  $K_2S_2O_8$  at time zero, without introducing a significant error into the analysis.

### Rate Expression

It follows from the above that eq. (3) may be integrated analytically to obtain the predicted change of conversion  $X$  with time  $t$  as follows:



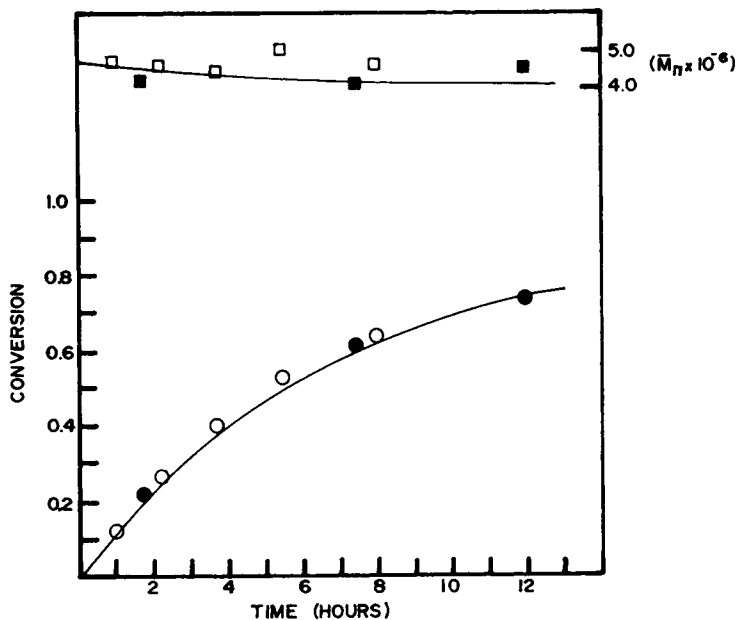


Fig. 11. Run (40-05-01).

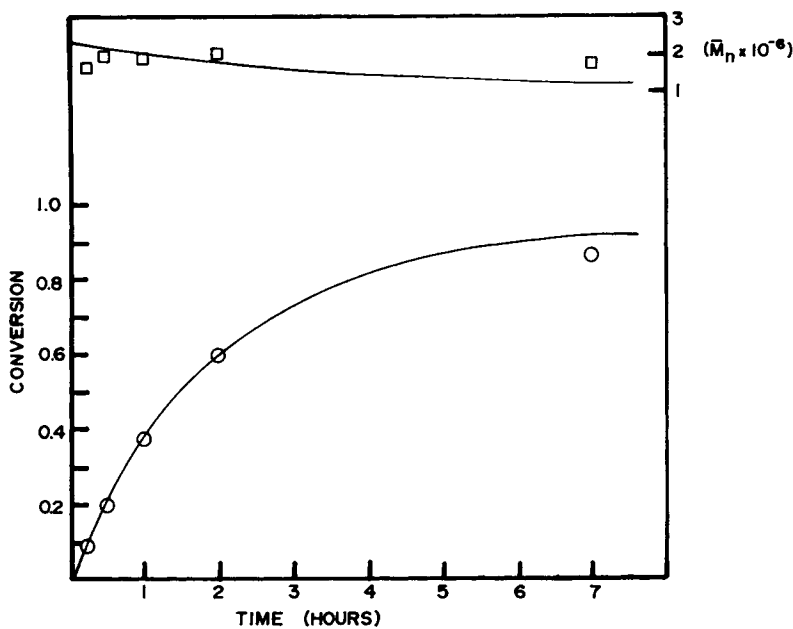


Fig. 12. Run (40-05-15).

$$X \equiv \frac{[M_0] - [M]}{[M_0]} = 1 - \left( \frac{k_{1.25}[I_0]^{0.50}[M_0]^{0.25}t}{4} + 1 \right)^{-4} \quad (6)$$

This equation was used, together with the appropriate values of  $k_{1.25}$  computed from eq. (4), to calculate the predicted conversion-time behavior represented

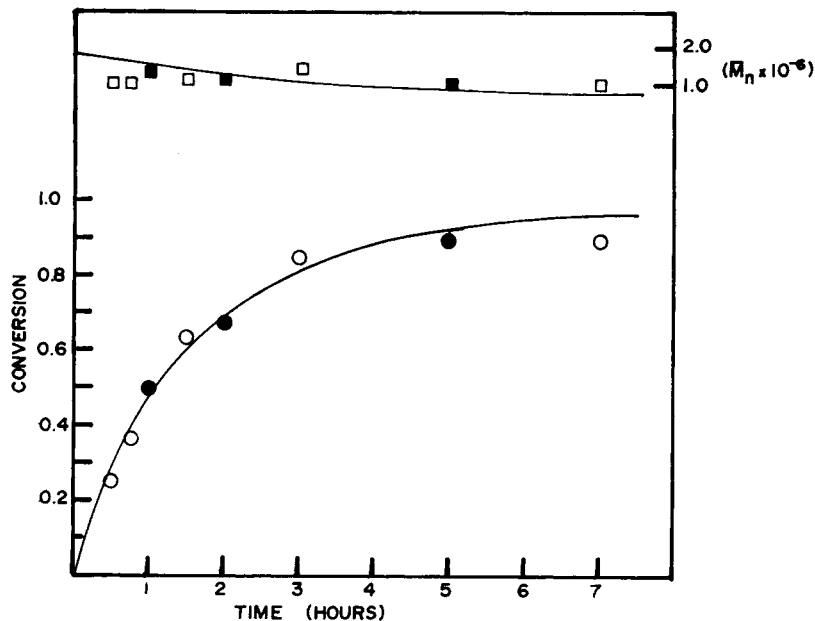


Fig. 13. Run (40-05-25).

by the curves on the lower parts of Figures 2 to 13. It is clear that satisfactory agreement exists between these predicted values and the measured experimental results. Therefore, eq. (3) has been confirmed as a valid expression for the polymerization rate  $R_p$  under the present experimental conditions.

### Transfer Constants

Substituting the expression for  $R_p$  from eq. (3) into eq. (1) and replacing  $[I]$  by  $[I_0]$ , the following expression for the instantaneous number-average chain length as an explicit function of conversion  $X$  is obtained:

$$\frac{1}{\bar{r}_n} = \frac{k_t}{k_p^2} k^{1.25} \frac{[I_0]^{0.50}}{[M_0]^{0.75}} \frac{1}{(1-X)^{0.75}} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p} \frac{[I_0]}{[M_0]} \frac{1}{1-X} \quad (7)$$

The molecular weight measured experimentally is the cumulative average for all polymer molecules formed up to conversion  $X$ . This is given by the following expression:

$$\left[ \frac{1}{\bar{r}_n} \right]_{\text{cum}} = \frac{1}{X} \int_0^X \frac{1}{\bar{r}_n} dx \quad (8)$$

Substituting for the instantaneous  $1/\bar{r}_n$  from eq. (7), eq. (8) may be integrated to give

$$\left[ \frac{1}{\bar{r}_n} \right]_{\text{cum}} = 4 \frac{k_t}{k_p^2} k^{1.25} \frac{[I_0]^{0.50}}{[M_0]^{0.75}} \frac{1 - (1-X)^{0.25}}{X} + \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p} \frac{[I_0]}{[M_0]} \frac{\ln[1/(1-X)]}{X} \quad (9)$$

Equation (9) may be written as

$$Y = \frac{k_{fm}}{k_p} + \frac{k_{fi}}{k_p} Z \quad (10)$$

where

$$Y = \left[ \frac{1}{\bar{r}_n} \right]_{\text{cum}} - 4 \frac{k_t}{k_p^2} k^{1.25} \frac{[I_0]^{0.50}}{[M_0]^{0.75}} \frac{1 - (1 - X)^{0.25}}{X} \quad (11)$$

and

$$Z = \frac{[I_0]}{[M_0]} \frac{\ln [1/(1 - X)]}{X} \quad (12)$$

Evidently, the free-radical polymerization model predicts, for this particular case, a linear relationship between variables  $Y$  and  $Z$ . The slope of the line is the ratio  $k_{fi}/k_p$ , and the intercept is  $k_{fm}/k_p$ . This allows the use of the linear least-squares method to estimate these parameters. However, one of the assumptions made to justify the use of this linear regression method is that the independent variable,  $Z$  in eq. (10), takes known and fixed values, whereas all the experimental errors are in the values of the dependent variable  $Y$ . This assumption can be justified in the present case because the error inherent in measuring the conversion  $X$ , and hence in estimating  $Z$  from eq. (12), is much smaller than that inherent in measuring the intrinsic viscosity extrapolated to high shear rates  $[\eta]_{\infty}$ , using it to estimate the average molecular weight from eq. (5) then calculating  $Y$  from eq. (11).

It may be noted that previous investigators have invariably used the differential expression for the molecular weight average, eq. (1), to estimate the transfer constants, with  $R_p$ ,  $[M]$ , and  $[I]$  taken at their original values at zero conversion. This permits the use of only one point for each experimental run, viz., that at zero conversion. On the other hand, the use of the integrated expression for the cumulative average chain length, eq. (9), permits the use of molecular weight data obtained at all conversion levels, hence provides more accurate estimators for the transfer constants.

Table III summarizes the results obtained by applying the method of least squares to eq. (10).<sup>15</sup> The confidence intervals shown in this table are calculated at 95% confidence level.

Confidence intervals for the parameters  $k_{fm}/k_p$  and  $k_{fi}/k_p$  were also calculated at progressively higher confidence levels to find out at which level each of these intervals will encompass zero and hence be statistically insignificant. This is an identical test as that provided by the "extra sum of squares principle."<sup>15</sup> It was found that  $k_{fi}/k_p$  at 25°C begins to be insignificant at 99.9% confidence level, whereas the other three estimators listed in Table III remain statistically sig-

TABLE III  
Least-Squares Estimators of the Transfer Constants

	$T = 25^\circ\text{C}$	$T = 40^\circ\text{C}$
$k_{fm}/k_p$	$7.86 \times 10^{-6} \pm 1.07 \times 10^{-6}$	$1.20 \times 10^{-5} \pm 3.28 \times 10^{-6}$
$k_{fi}/k_p$	$4.12 \times 10^{-4} \pm 2.38 \times 10^{-4}$	$2.63 \times 10^{-3} \pm 7.08 \times 10^{-4}$
Residual sum of squares	$2.62 \times 10^{-10}$	$2.23 \times 10^{-10}$
Residual variance	$6.55 \times 10^{-12}$	$5.71 \times 10^{-11}$
Correlation coefficient	-0.670	-0.686

nificant even beyond that confident level. Therefore, it was concluded that both the transfer reaction to monomer and that to initiator do occur in this polymerization system.

### Comparison of Measured and Predicted Molecular Weights

The values of the transfer constants listed in Table III were used to calculate the predicted number-average molecular weights as a function of conversion from eq. (9). The predicted  $\bar{M}_n$  are shown in the upper parts of Figures 2 to 13. From these figures it is clear that the agreement is satisfactory between the predicted values of  $\bar{M}_n$  and the experimentally determined ones except for run No. (25-05-01), where the predicted  $\bar{M}_n$  values are uniformly smaller than those measured experimentally. A possible explanation of this discrepancy lies in the fact that the polymers formed during this run had the highest intrinsic viscosities. But eq. (5) used to calculate  $\bar{M}_n$  from  $[\eta]$  was developed using polyacrylamides with  $\bar{M}_n$  less than one million.<sup>16</sup> Therefore, it would be expected that the error incurred by the use of this equation to estimate  $\bar{M}_n$  will be the largest for the high molecular weight polymers formed in run No. (25-05-01). In addition, due to the extreme curvature of the viscosity–shear rate data for the solutions of these high molecular weight polymers, as has been shown in our previous publication, the error introduced by extrapolating the flow data to high shear rates will be maximum for these polymers. It has also been observed by several investigators studying the flow properties of high polymers<sup>17–19</sup> that the logarithmic dependence of the apparent viscosity of a polymer solution on the molecular weight of the polymer at a fixed concentration was linear up to a critical molecular weight above which the straight line showed a sudden break and increased in slope. This was generally attributed to the onset of polymer chain “entanglements.” If the line describing the viscosity–molecular weight relationship below the critical molecular weight is extrapolated to the region above the critical molecular weight, it will predict, for any particular viscosity, a molecular weight that is larger in value than the true molecular weight. Such a phenomenon would explain the fact that the experimental  $\bar{M}_n$  calculated from viscosity measurements for the high molecular weight polymers formed during run No. (25-05-01) were higher than predicted by the model. However, additional data are clearly needed to confirm this argument.

### Comparison of the Transfer Constants with the Literature Values

The value of  $k_{fi}/k_p$  to  $K_2S_2O_8$  is being reported here for the first time. The present value of  $4.12 \times 10^{-4}$  at 25°C may be compared with the value of the corresponding transfer constant to  $H_2O_2$  reported to be  $5 \times 10^{-4}$  at 25°C by Dainton and Tordoff.<sup>8</sup>

From the values of  $k_{fm}/k_p$  listed in Table III, the overall activation energy for this ratio was found to be 5.24 kcal/mole. Extrapolation to 50 and 60°C yields values for  $k_{fm}/k_p$  equal to  $1.56 \times 10^{-5}$  and  $2.0 \times 10^{-5}$ , respectively. Comparing these values, together with those originally found at 25 and 40°C, with those reported in the literature (Table I), it is clear that the only close agreement is with the value of  $k_{fm}/k_p$  reported by Ishige<sup>13</sup> to be  $1.45 \times 10^{-5}$  at 50°C. But it has been shown in our previous publication that because of the dimensions of

the capillary viscometers used by Ishige to measure the viscosities of his polymer solutions, the conditions were such that his calculated intrinsic viscosities fortuitously approximated those presently obtained by extrapolating the flow data to high shear rates. Therefore, the only investigator for whom we could ascertain that the shear conditions were close to those used here, the estimated  $k_{fm}/k_p$  was almost identical to the one presently found. This demonstrates the influence of the shear conditions under which the intrinsic viscosities are measured on the ultimate kinetic results. Unfortunately, not enough information was available to evaluate the shear conditions at which the rest of the investigators listed in Table I operated.

Apart from the possible effect of the shear rate conditions on the measured intrinsic viscosities, these discrepancies may also be explained by the following observations:

1. The previous investigators chose to use the differential expression for the average chain length, eq. (1), to estimate the transfer constants. Therefore, a very limited set of data was available to fit the equation, viz., one observation per experimental run. For example, Dainton and Tordoff<sup>8</sup> used five data points to estimate the two transfer constants  $k_{fm}/k_p$  and  $k_{fi}/k_p$ , whereas Ishige and Hameilec,<sup>13</sup> Cavell and Gilson,<sup>10</sup> and Kwangfu<sup>12</sup> used eight, seven, and six points, respectively. With the considerable scatter usually associated with the molecular weight measurements, the confidence intervals on the values of the transfer constants estimated from such a limited set of data will be wide. This means that some overlap may be present between their confidence intervals and the present ones, which would eliminate some of the discrepancy mentioned above. It may be noted that in the present case, 42 and 41 data points were used to estimate the transfer constants at 25 and 40°C, respectively, due to the use of the integrated expression for the average chain length, eq. (9).

2. Some of the previous investigators<sup>8-10</sup> chose to use the following empirical equation, developed by Scholtan,<sup>20</sup> to estimate the weight-average molecular weights  $\bar{M}_w$  of their polyacrylamides:

$$[\eta] = 6.31 \times 10^{-5} \bar{M}_w^{0.80} \quad (13)$$

$\bar{M}_w$  was then divided by 2.0 to estimate a value for the number-average molecular weight  $\bar{M}_n$ . However, in the present investigation, as in several previous ones,<sup>5,7,12,13</sup>  $\bar{M}_n$  was calculated directly from eq. (5). In the molecular weight range investigated here, the discrepancy between the values of  $\bar{M}_n$  estimated by these two methods increases with increasing  $[\eta]$ , with eq. (13) giving the smaller estimate of  $\bar{M}_n$ . And, as is evident from eq. (1), smaller values for  $\bar{M}_n$  lead to larger values for  $k_{fm}/k_p$ . This is actually the case for the  $k_{fm}/k_p$  values reported by these investigators.

## CONCLUSIONS

An experimental investigation was carried out on the polymerization of acrylamide in water with potassium persulfate initiator under such conditions that the polymers produced had a number-average molecular weight in excess of one million. The present experimental rate data were found to agree quite well with the empirical rate expression proposed by Riggs and Rodriguez.<sup>7</sup>

Molecular weight averages were measured by viscometry. Shear rate effects

were accounted for by extrapolation to high shear rates where the polymer solutions approximated Newtonian behavior.

Values for the transfer constants to the acrylamide monomer and to the persulfate initiator were estimated at 25 and 40°C. Both transfer reactions were found to be statistically significant up to a confidence level of 99.9%.

The values reported here for  $k_{fm}/k_p$  were found to be generally smaller than those reported in the literature at the same temperatures. However, the present value for this constant extrapolated to 50°C was found to be in excellent agreement with that reported by Ishige and Hamielec,<sup>13</sup> whose viscometers closely approximated the shear conditions employed in the present investigation.

The above observation points to the need for a uniform and standard method to account for the non-Newtonian behavior of the polyacrylamide solutions. Such a method has been proposed in our previous publication and was used in the present one to evaluate the transfer constants. It was also found that, in comparing the values of the transfer constants reported by different investigators, the difference in the expressions used to compute the molecular weight averages from the intrinsic viscosities must be taken into account.

Finally, the use of an integrated expression for the molecular weight average, such as eq. (9), to estimate the transfer constants makes possible the utilization of the molecular weight data obtained at all conversion levels for parameter estimation. Furthermore, this practice eliminates the need for molecular weight data collected at extremely low conversion levels that are necessary to fit differential-type expressions, such as eq. (1). In such data the relative error introduced by the presence of small amounts of impurities in the reaction mixture would be maximum.

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