

Kinetic Study of Radical Polymerization. III. Solution Polymerization of Acrylamide by $^1\text{H-NMR}$

Ali-Reza Mahdavian,¹ Mahdi Abdollahi,¹ Hamid Reza Bijanzadeh²

¹Polymer Science Department, Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran

²Chemistry Department, Tarbiat Modares University, P.O. Box 14115/175, Tehran, Iran

Received 30 April 2003; accepted 16 March 2004

DOI 10.1002/app.20649

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Solution and radical polymerization of acrylamide in the presence of potassium persulfate in D_2O was investigated up to high conversion by high-field $^1\text{H-NMR}$ spectroscopy. The kinetics of reaction was studied according to the data obtained from the corresponding spectra at various times during the polymerization reaction progress. Processing of the data led us to derive the rate equation of this polymerization reaction and determine the reaction order of each component in the rate equation. The order, with respect to initiator, was consistent with the classical kinetic rate

equation (0.45), whereas the order with respect to monomer was greater than unity (1.49). The effect of temperature on the polymerization rate was also investigated and the activation energy of 48.4 kJ mol^{-1} was obtained over the temperature range of $60\text{--}75^\circ\text{C}$. Also some mechanistic studies were discussed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2007–2013, 2004

Key words: radical polymerization; $^1\text{H-NMR}$; acrylamide; kinetics (polym.); activation energy

INTRODUCTION

In recent years, environmental scientists have focused special attention to water-soluble polymers and tried to develop aqueous or solvent-free techniques to exclude environmentally hazardous organic solvents. Therefore, water-soluble polymers have been widely applied in several industries such as mineral processing, water treatment, and oil-well stimulation.¹

One of the most important water-soluble and synthetic polymers is polyacrylamide.² Polyacrylamide and its derivatives have been used extensively in electrophoresis, adhesives, oil-well stimulation, and paper reinforcement.³ According to the industrial importance of polyacrylamide, it is necessary to study its polymerization kinetic precisely, to optimize the polymerization process and control the characteristics of the final product.

Inverse-emulsion polymerization of acrylamide results in polymers with higher molecular weights, which are more applicable in oil recovery than those obtained by solution polymerization in water.⁴ Al-

though inverse-emulsion polymerization of acrylamide was previously studied in detail,^{4–7} solution polymerization of acrylamide in aqueous phase is still the major technique and has attracted particular attention.

Acrylamide, its growing radical, and corresponding polymer dissolve in water extremely well and the polymerization kinetics has been studied with different initiating systems such as: (1) thermal,^{8,9} (2) γ -irradiated,¹⁰ (3) ultrasonic,¹¹ and (4) photoinitiation.^{12,13}

Dainton et al.^{14,15} investigated polymerization kinetics of acrylamide in aqueous phase initiated by γ - and X rays and also its photoinitiation by hydrogen peroxide in the presence of ferric ions.¹⁶ Venkatarao and Santappa¹⁷ also studied photoinitiation of acrylamide in the presence of uranyl ion.

Redox systems for polymerization of acrylamide—such as chlorate–sulfite,¹⁸ persulfate–metabisulfite,¹⁹ Ce(III)-3-chloro-1-propanol,²⁰ ferric ion–bisulfite,²¹ hydrogen peroxide–hydroxylamine hydrogen chloride,²² Mn(III)–ethoxy acetic acid,²³ and persulfate–thiosulfate²⁴—were previously studied and applied.

Polymerization reactions using redox systems are generally more preferred than peroxy compounds alone because they initiate at lower temperatures and result in higher conversions. Therefore, they have been widely used in polymerization of acrylamide. Reported data in the literature, including kinetic studies of radical polymerization of acrylamide in aqueous phase, are limited to low conversions, specifically lower than 10% conversion.

Correspondence to: A.-R. Mahdavian (a.mahdavian@ippi.ac.ir).

Contract grant sponsor: Third World Academy of Sciences (TWAS), Trieste, Italy; contract grant number: RGA 01-094 RG/CHE/AS.

Contract grant sponsors: Iran Polymer and Petrochemical Institute (IPPI), Tehran; Tarbiat Modares University, Tehran.

Early reports on kinetic studies of persulfate-initiated polymerization of acrylamide in the aqueous phase were published by Riggs et al.,^{8,24} where the reaction progress was followed by a dilatometric technique. Recently Lin⁹ also investigated radical polymerization of acrylamide by potassium persulfate as initiator, up to higher conversions, by use of a gravimetric technique similar to Riggs's reaction conditions. In the dilatometry method, volumetric changes attributed to the large difference between monomer and polymer densities are recorded. This could be a good characteristic for detecting the progress of reaction. Although gravimetry is a simple and conveniently direct method in following polymerization reactions, it does not have sufficient precision, compared to the accuracy of recent instrumental analysis techniques. This comes from multiple steps used in gravimetric measurements (i.e., sampling and inhibition, precipitation, filtration, and drying) that cause wasting of the sample before weighing.

In this work we investigated—for the first time—the kinetics of acrylamide polymerization in the presence of potassium persulfate in D₂O by high-field ¹H-NMR spectroscopy. Processing of the obtained data led us to derive the rate equation of this polymerization reaction and determine the reaction order of each component in the corresponding rate equation. Here, a more precise technique was applied for this study compared to that reported by Riggs^{8,24} and Lin.⁹ Moreover, the principal data used in this kinetic study are more easily obtained, and characterized by higher accuracy, because of on-line data collection.

EXPERIMENTAL

Analytical grade acrylamide and potassium persulfate (KPS) were obtained from Merck Chemical Co. (Darmstadt, Germany) and used without further purification. Deuterium oxide (D₂O) as solvent was purchased from ARMAR Chemicals (Döttingen, Switzerland). The prepared solutions in NMR tubes were deaerated with argon gas (99.9% purity) to exclude oxygen from the solutions, which acts as a retardant in radical polymerization reactions.

Sample preparation and deaeration were performed at 0°C to inhibit reaction progress before inserting in the NMR chamber. All ¹H-NMR experiments reported in this study were carried out on a Bruker Avance 500 NMR spectrometer (Bruker Instruments, Darmstadt, Germany). The sample cavity was equilibrated at 60°C (i.e., the temperature at which the kinetic NMR experiments were carried out) by a BVT 3000 ($\pm 0.1^\circ\text{C}$) temperature control unit. After setting the cavity temperature at 60°C, the sample tube containing the reaction mixture was inserted into the sample chamber. The spectra were recorded at each 1-min time interval

until completion of reaction up to about 100% conversion.

All experimental data and amounts are recorded in Tables I–III.

RESULTS AND DISCUSSION

As a continuation of our previous research on the kinetic study of radical polymerization,^{25,26} we have applied the ¹H-NMR technique to follow the reaction progress.

¹H-NMR and ¹³C-NMR spectroscopic techniques are among the most useful methods to study both the kinetics and mechanisms of reactions. This is attributed to the high accuracy and precision of these techniques in on-line gain and recording of data relating to the progress of reaction. However, there are some limitations in the use of these spectroscopic techniques in certain cases, such as the following: (1) when the reaction rate is too high and greater than the scanning rate; (2) when the obtained product is insoluble and precipitates; and (3) when it is impossible to differentiate between the identical peaks of starting material and product and they overlap with each other. Of course ¹H-NMR spectroscopy is preferred over ¹³C-NMR because of its greater sensitivity and rate of data collection.

A ¹H-NMR spectrum of a mixture of acrylamide and polyacrylamide is shown in Figure 1. Chemical shifts of vinylic protons of acrylamide monomer appear in the range of 5.76–6.67 ppm and its splitting is completely ascribed to structure and geometry. After polymerization, chemical shifts of protons of aliphatic carbon in the polymer backbone appear at 1.74–2.60 ppm. Thus, the identical chemical shifts of monomer and polymer are sufficiently far from each other and their peak area provides a good scale for following quantitatively the progress of reaction with respect to kinetic aspects.

Kinetic studies at different monomer molar concentrations

In these series of experiments, the initiator concentration was kept constant and solutions with different amounts of acrylamide were prepared (Table I).

Additions and deaeration were carried out at 0°C to prevent preinitiation. NMR tubes containing the prepared samples were inserted in the NMR chamber, the temperature of which was set at 60°C. Scans were recorded at each 1-min time interval and some of them were plotted comparatively, as shown in Figure 2. It may be seen that at $t = 0$ min, there is no sign of polymer. After 22 min, all the monomers have almost been polymerized and only a trace of monomer exists, which means that the polymerization reaction has pro-

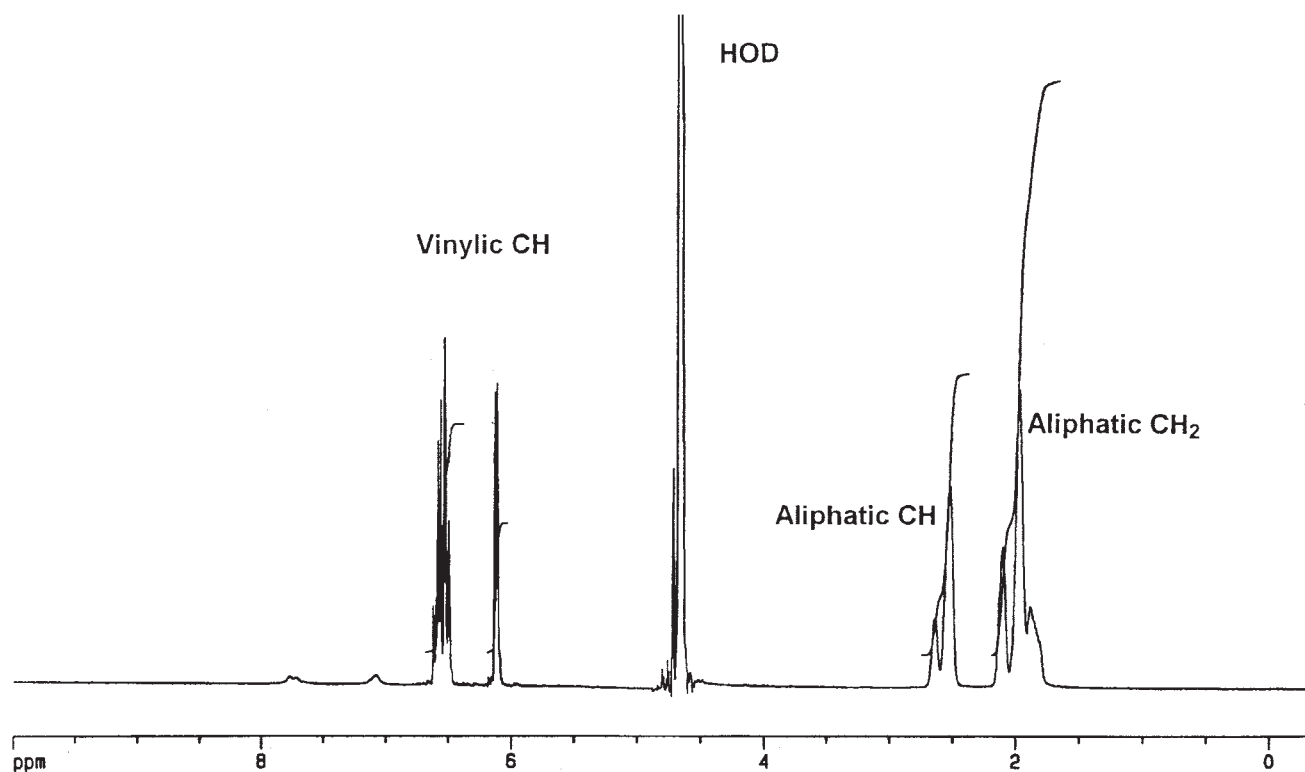


Figure 1 Typical $^1\text{H-NMR}$ spectrum of a mixture of acrylamide and polyacrylamide.

gressed up to high conversions ($\sim 100\%$) in only 22 min.

Comparison of the peak areas of monomer and polymer allowed us to calculate the amount of conversion, according to the following equation:

$$\pi = \frac{A_p}{A_p + A_m} \quad (1)$$

where π is the amount of conversion, A_p is the peak area of the obtained polymer, and A_m is the peak area of the monomer.

Variations of conversion versus time are plotted in Figure 3 for different samples. It is obvious that conversions up to about 90% could be obtained in the first 10 min of reaction progress.

TABLE I
Variation of Acrylamide Concentration at Constant Potassium Persulfate Concentration and Temperature

Run	Acrylamide (molar)	Potassium persulfate (molar)	Temperature ($^{\circ}\text{C}$)
A1	9.14×10^{-2}	4×10^{-2}	60
A2	1.91×10^{-1}	4×10^{-2}	60
A3	3.32×10^{-1}	4×10^{-2}	60
A4	4.78×10^{-1}	4×10^{-2}	60
A5	6.47×10^{-1}	4×10^{-2}	60
A6	8.82×10^{-1}	4×10^{-2}	60

By assuming the following rate equation [eq. (2)], the fraction of converted monomer could be applied to calculate the propagation rate:

$$R_p = -\frac{d[M]}{dt} = \frac{d\pi}{dt}[M_0] = k[M]^n[I]^p \quad (2)$$

where $[I]$ is the initiator concentration and $[M_0]$ is the primary monomer concentration.

The conversion rates were obtained from the slopes of the linear part of conversion–time graphs. Then, the rate of polymerization (R_p) was calculated by multiplying the conversion rate by the initial monomer concentration.

Figure 4 shows the plot of $-\log R_p$ versus $-\log[M]$. The slope of this plot reveals the order of reaction with respect to the monomer concentration. The amount of $n = 1.49$ for this polymerization reaction does not conform to that reported by Riggs et al. ($n = 1.25$)⁸ and Lin ($n = 1.26$).⁹

It should be noted that $^1\text{H-NMR}$ spectroscopy is a precise technique and our obtained data are thus undoubtedly accurate. This difference in the reaction order with respect to monomer concentration will be discussed below within the framework of some theories.

Kinetic studies at different initiator concentrations

Solutions with different amounts of potassium persulfate as initiator were prepared and the monomer con-

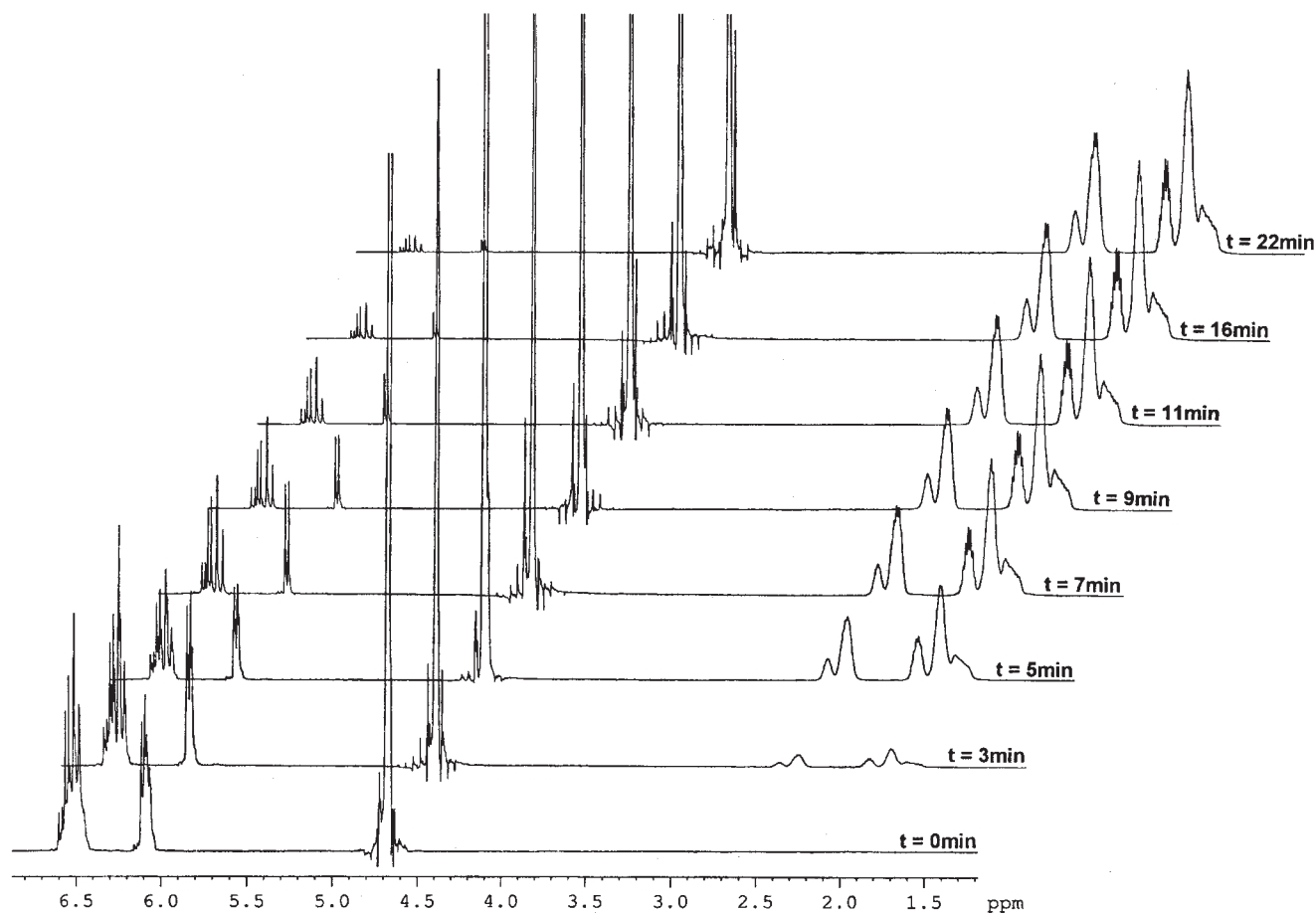


Figure 2 Comparative $^1\text{H-NMR}$ spectra of acrylamide polymerization at various times.

centration was kept constant (Table II). These series of experiments were performed because of conditions mentioned in both the previous section and the experimental section, except that the variable parameter was only initiator concentration.

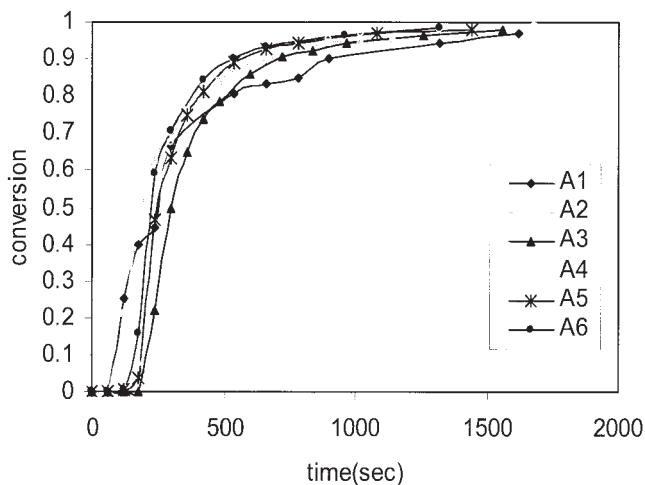


Figure 3 Curves relating to conversion versus time at different monomer concentrations.

According to the obtained results, variations of conversion versus time at different potassium persulfate concentrations were calculated (Fig. 5). The graphs show logically that the increase of initiator concentration causes the decrease in inhibition time.

Also the variation of $-\log R_p$ versus $-\log[I]$ is plotted in Figure 6 and its slope was determined. The

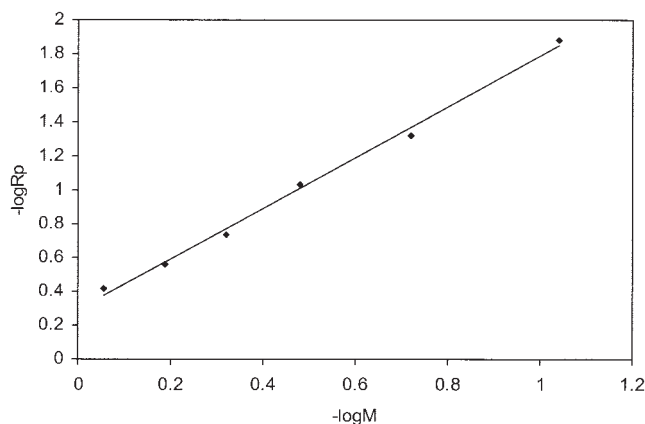


Figure 4 Plot of variation of $-\log R_p$ versus $-\log[M]$.

TABLE II
Variation of Potassium Persulfate Concentration at Constant Acrylamide Concentration and Temperature

Run	Acrylamide (molar)	Potassium persulfate (molar)	Temperature (°C)
B1	3.14×10^{-1}	6.28×10^{-3}	60
B2	3.14×10^{-1}	9.25×10^{-3}	60
B3	3.14×10^{-1}	1.37×10^{-2}	60
B4	3.14×10^{-1}	2.00×10^{-2}	60
B5	3.14×10^{-1}	4.00×10^{-2}	60
B6	3.14×10^{-1}	6.99×10^{-2}	60

obtained slope may be regarded as the order of reaction with respect to initiator concentration ($p = 0.45$).

The polymerization rate with respect to initiator concentration in this study is consistent with classical kinetic theory, which predicts the polymerization rate dependency on the square root of initiator concentration, as indicated in a number of studies.^{8,14-17,27,28}

Calculation of activation energy (E_a) and k_0

Three samples were prepared and polymerized at three different temperatures (Table III).

Variations of conversion versus time at three different temperatures are plotted in Figure 7. It is obvious that the polymerization reaction initiates earlier by increasing the reaction temperature and less time is needed to achieve higher conversions at higher temperatures.

By assuming the general rate equation [eq. (3)] and calculating $-\log R_p$ versus the reciprocal of absolute temperature (Fig. 8), k_0 may be calculated from the intercept and E_a may be determined from the line slope.

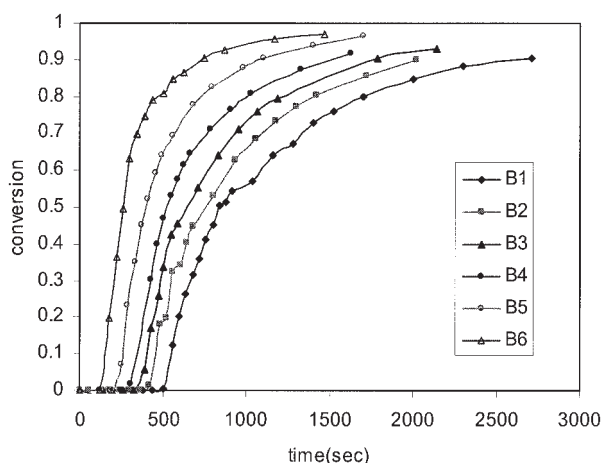


Figure 5 Curves relating to conversion versus time at different initiator concentrations.

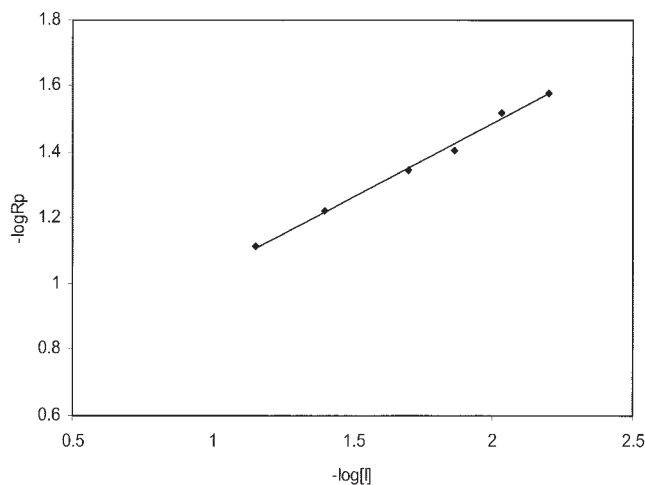


Figure 6 Plot of variation of $-\log R_p$ versus $-\log [I]$.

$$\log R_p = \log(k_0[M]^n[I]^p) - \left(\frac{E_a}{R}\right)\frac{1}{T} \quad (3)$$

where $[M]$ and $[I]$ are considered constant.

Correspondingly, the E_a value of solution and radical polymerization of acrylamide in the presence of potassium persulfate was obtained: 48.4 kJ mol^{-1} . The calculated E_a value was about the same as that reported by Lin.⁹

The k_0 value obtained for this polymerization reaction from eq. (3) and Figure 8 was $6.81 \times 10^7 \text{ L mol}^{-1} \text{ min}^{-1}$, which was also verified by calculating the k -value from eq. (2). The number of intercepts in Figures 4 and 6 allowed us to determine the k -value at two different conditions. The above average value, obtained E_a , and definite temperature could be applied to calculate k_0 . The k_0 value obtained by the second method was $7.01 \times 10^7 \text{ L mol}^{-1} \text{ min}^{-1}$, which was about the same as that calculated directly from eq. (3). This confirms our calculation method and accuracy of the reported k_0 value.

Mechanistic studies

There are three theoretical treatments to explain solution-catalyzed radical polymerization, in which the dependency on monomer concentration is greater

TABLE III
Variation of Temperature at Constant Potassium Persulfate and Acrylamide Concentrations

Run	Acrylamide (molar)	Potassium persulfate (molar)	Temperature (°C)
C1	1.98×10^{-1}	9.02×10^{-3}	60
C2	1.98×10^{-1}	9.02×10^{-3}	67
C3	1.98×10^{-1}	9.02×10^{-3}	75

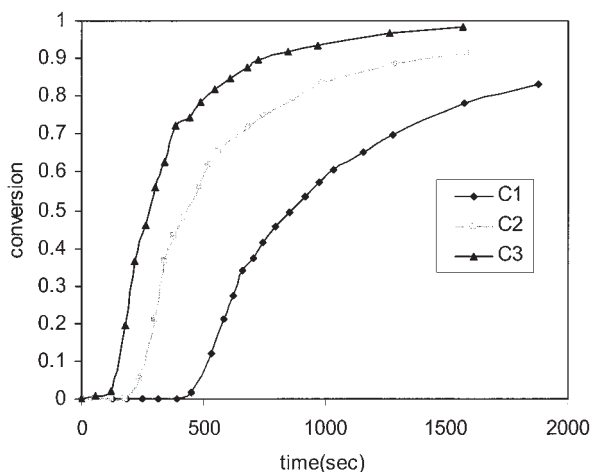


Figure 7 Curves relating to conversion versus time at different temperatures.

than first-order: (1) the complex theory, (2) the cage-effect theory, and (3) the solvent-transfer theory. These were previously reviewed in the literature.^{29,30} It should be noted that the solvent-transfer theory may be disregarded in this work. This is explained by the fact that hydroxyl (or deuterioxyl) radicals are very reactive toward acrylamide monomer and have no retardation effect on the polymerization reaction of acrylamide. Thus our major discussion will focus on the other two theories.

It is noteworthy that the increase in the order of reaction rate relative to monomer concentration means that the monomer may encounter the initiation process through different mechanisms, such as the effect of monomer on the initiator efficiency and induced decomposition of the initiator.³¹ This causes the dependency of polymerization rate on monomer concentration to exceed unity.

In the complex theory, formation of a complex between monomer and initiator (persulfate) is the key step and substantially alters the activation energy. In other words, if the complexation is carried out, the activation energy will be greater than that of a similar reaction that conforms to the cage-effect theory. By comparison of our calculated E_a (close to that reported by Lin⁹) and the value of E_a obtained by Riggs (70.6 kJ mol⁻¹), it is clear that our calculated E_a (48.4 kJ mol⁻¹) is much less than that of Riggs et al.⁸ Thus the controlling mechanism in our reaction condition will be in accordance with the cage-effect theory.

Some noticeable reactions attributed to the polymerization reaction are summarized as follows:

- $S_2O_8^{2-} \xrightarrow{k_1} (2SO_4^-)$ (Solvent-caged initiating radical)
- $(2SO_4^-) \xrightarrow{k_2} S_2O_8^{2-}$

- $(SO_4^-) + M \xrightarrow{k_3} M^*$
- $(SO_4^-) + H_2O \xrightarrow{k_4} HSO_4^- + HO^*$
- $(SO_4^-) \xrightarrow{k_5} SO_4^{\cdot-}$
- $M_n + M \xrightarrow{k_6} M_{n+1}$ (Propagation)
- $M_n + M_p \xrightarrow{k_7} P_{n+p}$ (Termination)

The general rate equation, with respect to some conventional assumptions, is

$$R_p = k_6 \left(\frac{2k_1}{k_7} \right)^{1/2} [S_2O_8^{2-}]^{1/2} \times \left(\frac{k_3[M] + k_4 + k_5}{k_3[M] + k_4 + k_5 + k_2} \right)^{1/2} [M] \quad (4)$$

The steps characterized by $k_4 + k_5$, k_2 , and $k_3[M]$ represent the escape of primary radicals from the solvent cage. To simplify eq. (4), we posit the following two assumptions:

1. If $k_4 + k_5 \gg k_3[M]$, then the rate will be first-order with respect to monomer concentration.
2. If $k_4 + k_5 \ll k_3[M]$, then the rate will be dependent on monomer concentration, with an order of 1.5, according to the following equation:

$$R_p = k_6 \left(\frac{2k_1}{k_7} \right)^{1/2} [S_2O_8^{2-}]^{1/2} \left(\frac{k_3}{k_3[M] + k_2} \right)^{1/2} [M]^{3/2} \quad (5)$$

Here, the dependency on monomer concentration varies by a power of 1.0 to 1.5 with respect to conditions such as concentration.

The above second assumption conforms to our experimental data with respect to the order of monomer in the corresponding rate equation.

Rearrangement of eq. (5) yields

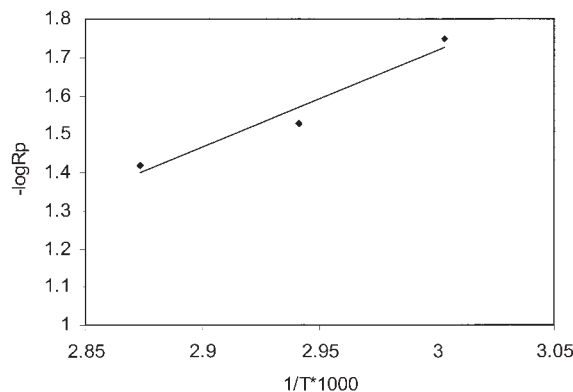


Figure 8 Plot of eq. (3) for variation of $-\log R_p$ versus $(1/T) \times 1000$.

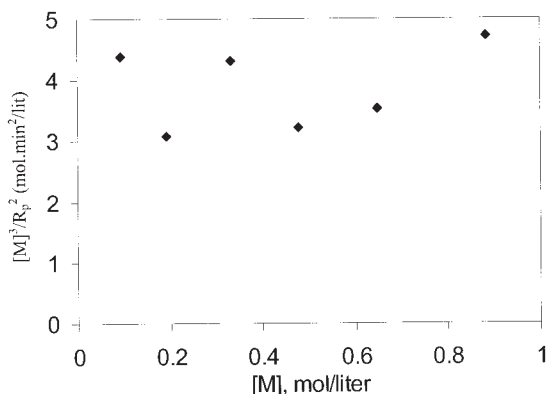


Figure 9 Plot of eq. (6) for variation of $[M]^3/R_p^2$ versus $[M]$.

$$\frac{[M]^3}{R_p^2} = \frac{k_7}{Kk_6^2(2k_1)[S_2O_8^{2-}]} (1 + K[M]) \quad (6)$$

where $K = k_3/k_2$.

The graph relating to eq. (6) is shown in Figure 9. It may be observed that the slope of the best-fitting line passing through the points is approximately zero. Therefore, eq. (6) may be written as

$$\frac{[M]^3}{R_p^2} = \frac{k_7}{Kk_6^2(2k_1)[S_2O_8^{2-}]} \quad (7)$$

Equation (7) reveals a 3/2 dependency of polymerization rate on monomer concentration.

CONCLUSIONS

The $^1\text{H-NMR}$ spectroscopic technique is among the most useful methods for the study of kinetics and mechanism of reactions. This is attributed to the high accuracy and precision of this technique in on-line gain and recording of data relating to the progress of reaction. Solution and radical polymerization of acrylamide in the presence of potassium persulfate in D_2O was investigated to high conversion by high-field $^1\text{H-NMR}$ spectroscopy. The kinetics of reaction was studied according to the data obtained from the corresponding spectra at various times during progress of the polymerization reaction. Processing of the data led us to derive the rate equation of this polymerization reaction and determine the reaction order of each component in the rate equation, expressed as

$$R_p = -\frac{d[M]}{dt} = k[M]^{1.49}[I]^{0.45}$$

The effect of temperature on the polymerization rate was also investigated and the activation energy of 48.4

kJ mol^{-1} was obtained over the temperature range of 60–75°C. Mechanistic studies show that the governing mechanism may be semicaged in nature and the liberated radical initiators from the solvent cage are primarily propagating this fast polymerization reaction, which progresses up to 100% conversion in a reaction time of only about 22 min.

A.R.M. expresses his gratitude to Third World Academy of Sciences (TWAS) for financial support of this work (RGA 01-094 RG/CHE/AS). Also the support of Iran Polymer and Petrochemical Institute (IPPI) and Tarbiat Modares University is gratefully acknowledged.

References

- Kurenkov, V. F.; Mysgchenkov, V. A. *Eur Polym Mater* 1980, 16, 1229.
- George, M. H.; Ghosh, A. *J Polym Sci Polym Chem Ed* 1978, 16, 981.
- Inoue, Y.; Fukutomi, T.; Chujo, R. *Polym J* 1983, 15, 103.
- Candau, F.; Leong, Y. S.; Fitch, R. M. *J Polym Sci Polym Chem Ed* 1985, 23, 193.
- Vanderhoff, J. W.; DiStefano, F. V.; El-Aasser, M. S.; O'Leary, R.; Shaffer, O. M.; Visioli, D. L. *J Dispersion Sci Technol* 1984, 5, 323.
- Vanderhoff, J. W.; Visioli, D. L.; El-Aasser, M. S. *Polym Mater Sci Eng* 1986, 54, 375.
- Graillat, C.; Pichot, C.; Guyot, A.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1986, 24, 427.
- Riggs, J. P.; Rodriguez, F. *J Polym Sci Part A-1* 1967, 5, 3151.
- Lin, H.-R. *Eur Polym J* 2001, 37, 1507.
- Schulz, R.; Renner, G.; Henglein, A.; Kern, W. *Makromol Chem* 1954, 12, 20.
- Henglein, A. *Makromol Chem* 1954, 14/15, 128.
- Arbuzova, I. A.; Efremova, V. N.; Ulezlo, I. K. *Dokl Akad Nauk SSSR* 1957, 112, 645.
- Oster, G. K.; Oster, G.; Prati, G. *J Am Chem Soc* 1957, 79, 595.
- Collinson, E.; Dainton, F. S.; Mc Naughton, G. S. *Trans Faraday Soc* 1957, 53, 476.
- Collinson, E.; Dainton, F. S.; Mc Naughton, G. S. *Trans Faraday Soc* 1957, 53, 499.
- Dainton, F. S.; Tordoff, M. *Trans Faraday Soc* 1958, 53, 666.
- Venkatarao, K.; Santappa, M. *J Polym Sci Part A-1* 1967, 5, 637.
- Suen, T. J.; Sen, Y.; Lockwood, J. V. *J Polym Sci* 1958, 31, 481.
- Rodriguez, F.; Givey, R. D. *J Polym Sci* 1961, 55, 713.
- Mino, G.; Kaizerman, S.; Rasmussen, E. *J Polym Sci* 1959, 38, 393.
- Talamini, G.; Turolia, A.; Vianello, E. *Chem Ind (Milan)* 1953, 45, 335.
- Kay, T. A.; Rodriguez, F. *J Appl Polym Sci* 1983, 28, 633.
- Balakrishnan, T.; Subbu, S. *J Polym Sci Part A: Polym Chem* 1986, 24, 2271.
- Riggs, J. P.; Rodriguez, F. *J Polym Sci A-1* 1967, 5, 3167.
- Mahdavian, A. R.; Zandi, M. *J Appl Polym Sci* 2003, 87, 2335.
- Mahdavian, A. R.; Zandi, M. *J Appl Polym Sci* 2003, 90, 1648.
- Ishige, T.; Hamielec, A. E. *J Appl Polym Sci* 1973, 17, 1479.
- Cavell, E. A. S. *Makromol Chem* 1962, 54, 70.
- Baford, C. H.; Barb, W. G.; Jenkins, A. D.; Onyon, P. F. *The Kinetics of Vinyl Polymerization by Radical Mechanisms*; Butterworths: London, 1958.
- Kolthof, I. M.; Medalia, A. I.; Raaen, H. P. *J Am Chem Soc* 1951, 73, 1733.
- Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981; Chapter 3, pp. 200–201.