Kinetic Study of the Aqueous Free-Radical Polymerization of 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid via an Online Proton Nuclear Magnetic Resonance Technique

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ABSTRACT: The free-radical polymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) in aqueous media and in the presence of potassium persulfate (KPS) as a thermal initiator was studied. The ^{1}H-NMR method was applied to record the reaction data in online gain. The effects of the monomer and initiator concentrations and also the reaction temperature were studied. The order of reaction with respect to the monomer was much greater than unity (1.94). None of the three theories describing an order of reaction higher than unity could predict the AMPS polymerization mechanism in this study. So, a new mechanism is presented. It is suggested that initiation took place through the formation of a complex between the initiator and monomer, and termination occurred not only by a bimolecular reaction but also by a monomolecular reaction. The order with respect to KPS was 0.49; this was consistent with classical kinetic theory. The determined activation energy at the overall rate of reaction was 92.7 kJ mol^{-1} K^{-1}. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: activation energy; initiators; kinetics (polym.); NMR

INTRODUCTION

In recent years, environmental scientists have been attracted to water-soluble polymers. The aqueous polymerization method was developed for the elimination of ecologically hazardous organic solvents.[1] Poly(2-acrylamido-2-methylpropane sulfonic acid) [poly(AMPS)] and its derivatives are often used as water-soluble polymers with various applications. These polymers are used extensively in a wide range of industrial products and processes, such as in food, cosmetics, paints pigments, thickeners, coatings, personal care products, adhesives, and inks.[2] Most of these polymers are produced by free-radical polymerization because of its advantages, which include simplicity and versatility.[3]

There are several techniques for calculating the rate constants and order of reactions in free-radical polymerization reactions. The most usual ones include differential scanning calorimetry,[4–6] gravimetry,[7] dilatometry,[8] NMR,[1,9] and pulsed-laser-initiated polymerization.[10,11]

Kinetic studies of the spontaneous polymerization of (meth)acrylamide, ethyl acrylamide, and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) have been reported by some researchers. These studies have revealed that the monomer concentration and degree of neutralization have an important role in the polymerization rate of the mentioned systems.[12,13]

Obtaining a high-molecular-weight polymer with uniform crosslinker incorporation, low residual monomer levels, and high production rates requires a detailed and precise knowledge of polymerization kinetics.[14] Hence, according to the industrial application of poly(AMPS), it is necessary to study its polymerization kinetics precisely to optimize the polymerization process and control the characteristics of the final product.

Beuermann et al.[15] investigated the kinetics in an aqueous solution of AMPS via pulsed-laser-initiated polymerization and calculated the individual rate constants in photoinitiation conditions. However, no data were available for the order of reaction in the aqueous polymerization of AMPS.

In this study, for the first time, the kinetics of AMPS polymerization in the presence of potassium persulfate (KPS) in D$_2$O were investigated by ^{1}H-NMR spectroscopy. The order of reaction of each component in the corresponding rate equation was determined. The activation energy (E_a) was calculated for the aqueous polymerization of AMPS, too.

EXPERIMENTAL

Materials

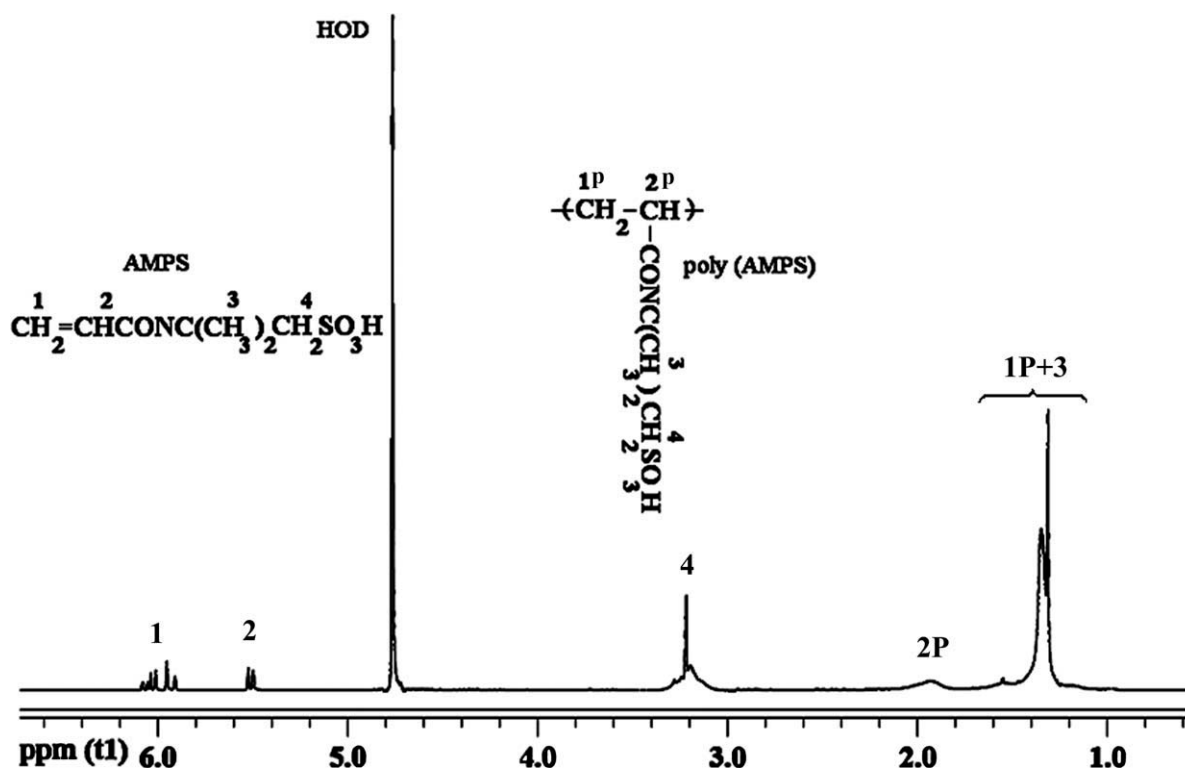AMPS and KPS were purchased from Fluka, Germany and Merck, Germany, respectively, and were

Figure 1 ^{1}H-NMR spectrum of AMPS and poly(AMPS). HOD demonstrates deuterium water.

recrystallized from ethanol for further purification. D_2O as a solvent was obtained from ARMAR Chemicals (Switzerland).

Online ^{1}H-NMR kinetic experiments

In this study, ^{1}H-NMR experiments were carried out on a Bruker Avance 400 MHZ instrument (Germany). At first, a sample containing the reaction mixture, solvent, monomer, and initiator, which was purged with nitrogen to remove dissolved air, was introduced into a sample cavity and allowed to calibrate. Then, the sample tube was sent out. After the cavity was set at the desired temperature (by a BVT 3200 temperature control unit, Germany), the sample tube was inserted into the sample chamber, and the start time was recorded. The spectra were recorded at 30–60 time intervals up to high conversions (>75%).

RESULTS AND DISCUSSION

Among the methods mentioned, NMR techniques seemed to be the most useful method for kinetic study in radical polymerization because of their high accuracy and precision, and the recorded data relates to the progress of the reaction in online gain. However, there are some restrictions in the application of these spectroscopic techniques. In cases such

as (1) a very high rate of reaction when it is greater than scanning rate, (2) the overlapping of the peaks of reactants and obtained product, and finally, (3) the precipitation of the obtained product, this method is not convenient.[1]

Among different NMR techniques, ^{1}H-NMR was preferred over ^{13}C-NMR because of its greater sensitivity, higher rate of data collection, and ability to use smaller diameter tubes, which helped in maintaining isothermal conditions.[1] The ^{1}H-NMR spectra of AMPS and poly(AMPS) are shown in Figure 1. Through the improvement of the polymerization reaction, vinylic protons of the monomer [Figs. 1(a–f) and 2(a,b)] were decreased, and the aliphatic peaks of the polymers (1 and 2) were produced. Monomer conversion was calculated by Mahdavian et al.[1] according to following equation:

$$\pi = \frac{A_p}{A_p + A_m} \tag{1}$$

where π, A_p, and A_m are the monomer conversion and peak areas of the polymer and monomer, respectively.

Because peaks 1 and 3 overlapped each other (Fig. 1), the measurement of the exact amount of monomer conversion by the previous equation was quite hard. So, peak 4 was selected as a reference ($A_4 = 1$), and the other peak areas were calculated according to that. The amount of monomer conversion at a
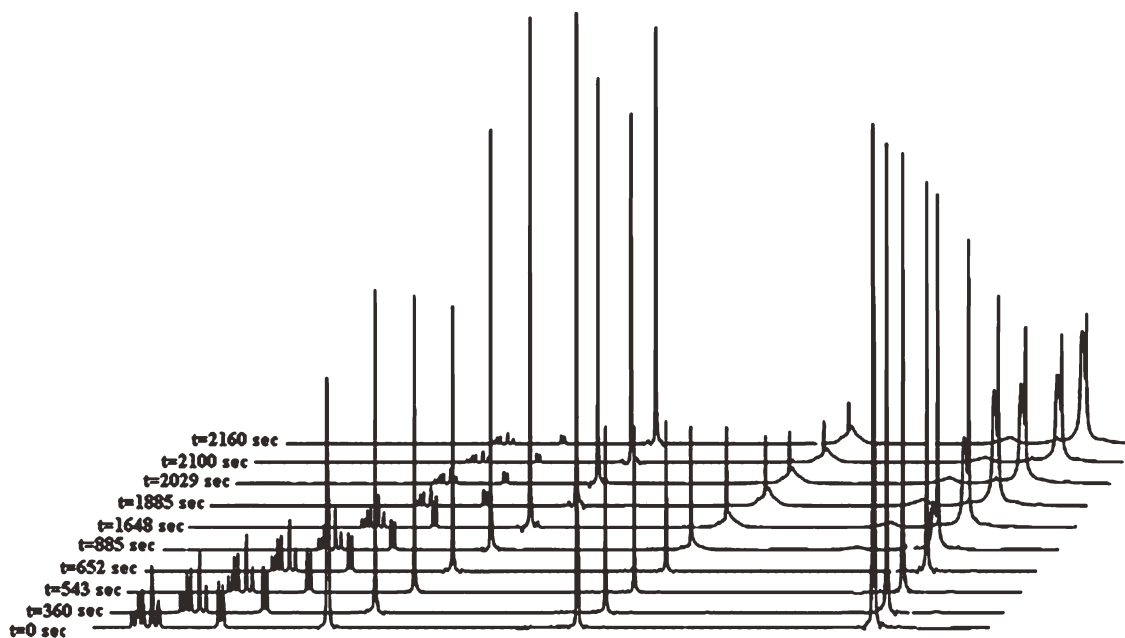
Figure 2 Relative ^{1}H-NMR spectra of AMPS polymerization at different times (t's).

specific time was determined by Eq. (2) (where A is the peak area 1):

$$\Pi = 1 - \frac{A}{A_4} \text{ or } \Pi = 1 - A \qquad (2)$$

where Π is the monomer conversion at a specific time.

NMR kinetic analysis at different initiator concentrations

The monomer molar concentration was kept constant, and solutions with various amounts of initiator were prepared. The formulations used in this series of experiments are presented in Table I. The polymerization temperature was set at 40°C and was kept constant in these reactions. A typical ^{1}H-NMR spectrum of sample 10 is shown in Figure 2. Variations of conversion versus time are plotted in Figure 3. This figure reveals that induction time decreased with increasing initiator amount in the polymerization system.

To estimate the order of reaction, the following equation was applied:[1]

TABLE I
Variation of the KPS Molar Concentration at a Constant AMPS Amount and Temperature

Sample number	[AMPS]$_0$ (mol/L)	[KPS]$_0$ (mol/L)	T (°C)	Induction time (s)
1	0.773	0.044	40	398
2	0.773	0.066	40	235
3	0.773	0.096	40	190
4	0.773	0.143	40	170

$$R_p = -\frac{d[\text{M}]}{dt} = \frac{d\Pi}{dt}[\text{M}_0] = k[\text{M}]^n[\text{I}]^p \qquad (3)$$

where R_p, [I], [M], and [M$_0$] are the polymerization rate, initiator and monomer concentrations, and initial concentration of the monomer, respectively. With a constant initial monomer content, the slope of $-\log R_p$ versus $-\log$ [I] showed the order of reaction with respect to the initiator concentration. Corresponding to Figure 4, the calculated amount of p was 0.48. The polymerization rate in classical kinetic theory depends on the square root of the initiator concentration.[1] So, the obtained result showed good agreement with classical kinetic theory.
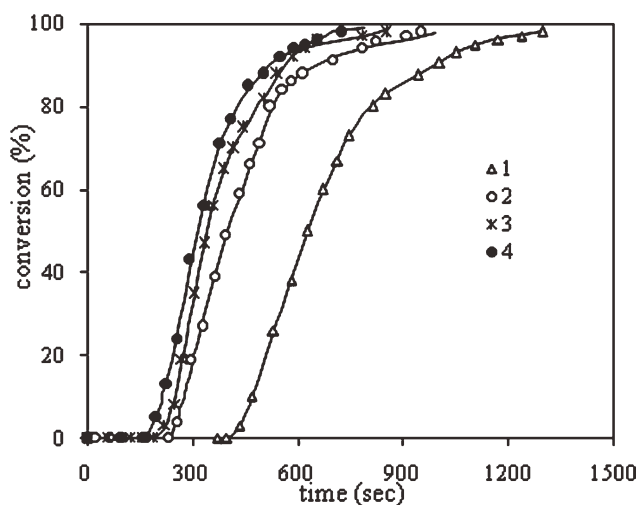

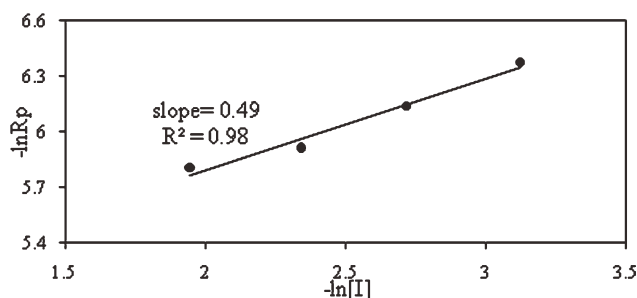**Figure 3** Monomer conversion versus time at different initiator contents.

Figure 4 Variation of $-\log R_p$ versus $-\log [I]$.

NMR kinetic analysis at different monomer concentrations

Solutions with different monomer molar concentrations and a constant amount of initiator were prepared (Table II). It is necessary to mention that polymerization reactions were allowed to proceed at the same temperature at which the reactions were carried out at a constant amount of monomer. The variation of conversion is demonstrated in Figure 5. The n value determined by the slope of $-\log R_p$ versus $-\log [M]$ (Fig. 6) was 1.94. In the polymerization of acrylamide, an order of 1.49 was acquired.[1] This result shows that AMPS was much more sensitive to the monomer content than acrylamide because of the greater ionic strength resulting from its sulfonic group.

Determination of k_0 and E_a

A general rate of polymerization was assumed by Eq. (4):

$$R_p = k_0[M]^n[I]^p e^{-\frac{E_{a1}}{RT}} \text{ or } \ln R_p = \ln(k_0[M]^n[I]^p) - \left(\frac{E_a}{R}\right)\frac{1}{T} \tag{4}$$

where E_a is the overall activation energy of polymerization. R and T are ideal gas constant and polymerization temperature, respectively. k, n and p show overall rate constant of polymerization, order of reaction based on monomer, order of reaction based on initiator, respectively. The variation of the reaction rate with temperature is shown in Figure 7 (on the basis of the formulations presented in Table III). At constant amounts of monomer and initiator, the slope and intercept of the $-\ln R_p$ versus $1/T$ plot represented E_a and k_0, respectively (Fig. 8). The calculated amount of

TABLE II
Variation of the AMPS Molar Concentration at a Constant KPS Amounts and Temperatures

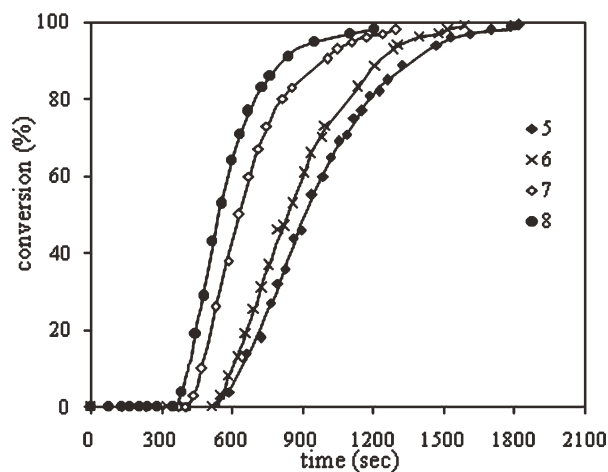| Sample number	[AMPS]$_0$ (mol/L)	[KPS]$_0$ (mol/L)	T (°C)	Induction time (s)
5	0.483	0.044	40	530
6	0.579	0.044	40	515
7	0.773	0.044	40	398
8	0.966	0.044	40	350

Figure 5 Monomer conversion versus time at different monomer contents.

E_a was 92.7 kJ mol^{-1} K^{-1}, and k_0 determined by the intercept of mentioned plot was 3.385×10^{13} mol L^{-1} s^{-1}. These were about the same as the values calculated from the intercepts of Figures 4 and 5.

Mechanistic study

According to previous studies, there are three theories that explain the dependence of the polymerization rate on monomer concentrations greater than first order: (1) solvent transfer theory, (2) cage effect theory, and (3) complex theory.[1,16]

Solvent transfer theory

Two species derived from the thermal decomposition of persulfate in water (deutroxyl) are capable of initiating polymerization, radical ion, and hydroxyl (deuteroxyl) radical.[17] In the presence of the monomer, the following reactions are expected (where the subscripts refer to the degree of polymerization):
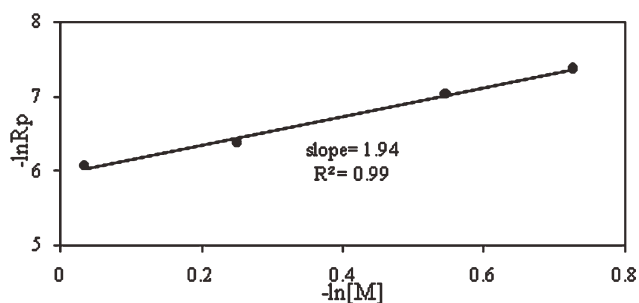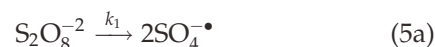
$$S_2O_8^{-2} \xrightarrow{k_1} 2SO_4^{-\bullet} \tag{5a}$$

$$SO_4^{-\bullet} + H_2O \xrightarrow{k_2} HSO_4^- + {}^{\bullet}OH \tag{5b}$$

$$SO_4^{-\bullet} + M \xrightarrow{k_{i1}} M^{\bullet} \tag{5c}$$

Figure 6 Variation of $-\log R_p$ versus $-\log [M]$.
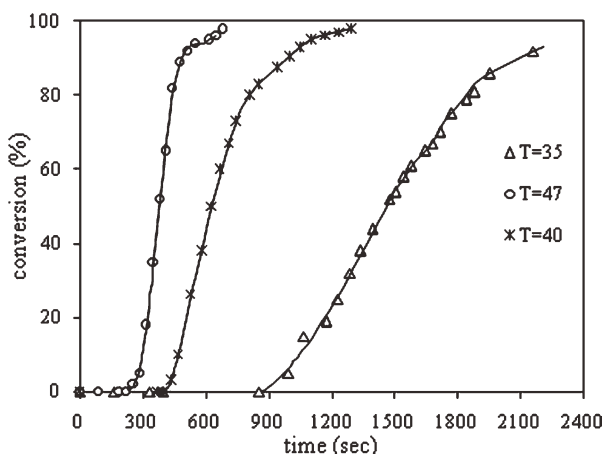
Figure 7 Monomer conversion versus time at various temperatures.

$$\bullet OH + M \xrightarrow{k_{i2}} M^\bullet \tag{5d}$$

$$M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet \tag{5e}$$

$$M_g^\bullet + M_k^\bullet \xrightarrow{k_t} P_{g+k} \tag{5f}$$
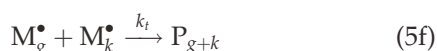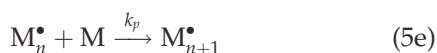
Derived sulfur-containing fragments from persulfate are very reactive toward monomers, and no data are available for the formation of hydroxyl (or deuteroxyl) free radicals in water.[16] The conditions $k_2 = 0$ and the reaction in eq. (5d) did not occur in this system. The general rate of polymerization showed a first-order dependence on the monomer concentration [Eq. (6)]:

$$R_p = k_p (2k_1/k_t)^{1/2}[S_2O_8^{-2}][M] \tag{6}$$

Hence, the solvent transfer theory was ignored in the aqueous free-radical polymerization of AMPS.

Cage effect theory

This theory is based on the formation of a barrier for the separation of sulfur-containing fragments from the surrounding solvent. The subsequent mechanisms are added in eqs. (5b)–(5f):
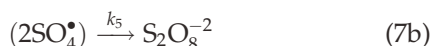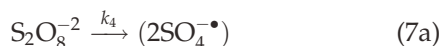
$$S_2O_8^{-2} \xrightarrow{k_4} (2SO_4^{-\bullet}) \tag{7a}$$

$$(2SO_4^\bullet) \xrightarrow{k_5} S_2O_8^{-2} \tag{7b}$$

TABLE III
Variation of the Temperature at Constant Amounts of Monomer and Initiator

Sample number	[AMPS]$_0$ (mol/L)	[KPS]$_0$ (mol/L)	T (°C)	Induction time (s)
9	0.773	0.044	40	398
10	0.773	0.044	35	890
11	0.773	0.044	47	230
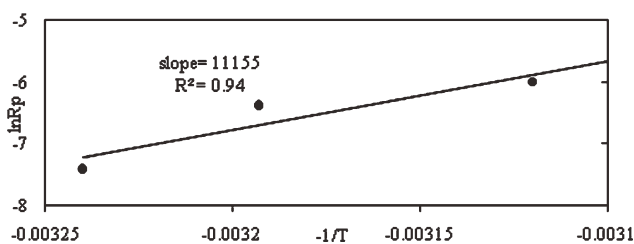
Figure 8 Variation of log R_p versus $-1/T$.

$$(SO_4^{-\bullet}) + M \xrightarrow{k_6} M^\bullet \tag{7c}$$

$$(SO_4^{-\bullet}) + H_2O \xrightarrow{k_7} HSO_4^- +^\bullet OH \tag{7d}$$

$$(SO_4^{-\bullet}) \xrightarrow{k_8} SO_4^{-\bullet} \tag{7e}$$

$$2SO_4^{-\bullet} \xrightarrow{k_9} S_2O_8^{-2} \tag{7f}$$
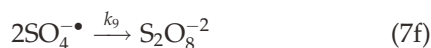
where the parentheses demonstrate fragments in a solvent cage. Through consideration of some assumptions, the polymerization rate can be described by Eq. (8):

$$R_p = k_p \left(\frac{2k_1}{k_t}\right)^{1/2}[S_2O_8^{-2}]^{1/2}\left(\frac{k_6[M] + k_7 + k_8}{k_6[M] + k_7 + k_8 + k_5}\right)^{1/2}[M] \tag{8}$$

The order of reaction corresponding to the monomer concentration depends on two competitive terms ($k_6[M]$ and $k_7 + k_8$). In the case of $k_7 + k_8 \geq k_6[M]$, the rate is first order according to the monomer. On the other hand, when $k_7 + k_8 \leq k_6[M]$, the dependence on the monomer varies from a power of 1.5 to 1.

As a result, cage effect theory could predict the dependence of the polymerization rate on the monomer concentration up to 1.5 with respect to conditions such as concentration.[17] However, in AMPS polymerization, the calculated order was more than that from cage effect theory. Thus, cage effect theory could not have been the controlling mechanism of the AMPS polymerization.

Complex theory

The formation of a complex between the monomer and initiator is proposed in complex theory, and the rate of complex decomposition is a determining factor in the initiation process:

$$S_2O_8^{-2} + M \xleftrightarrow{K_c} S_2O_8^{-2} - M \tag{9a}$$

$$S_2O_8 - M^{-2} \xrightarrow{k_3} M^\bullet + SO_4^{-\bullet} \tag{9b}$$
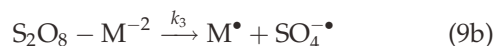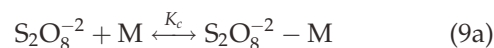
The complex concentration is given by Eq. (10):

$$[S_2O_8 - M^{-2}] = K_c[S_2O_8^{-2}][M]/(1 + K_c[M]) \tag{10}$$

Where K_c is the rate constant of complex formation of monomer with initiator. The general rate of polymerization, with respect to the usual assumptions, is given by Eq. (11):

$$R_p = k_p \left(\frac{2k_3}{k_t}\right)^{1/2} \left(\frac{K_c}{1 + K_c[\text{M}]}\right)^{1/2} [\text{S}_2\text{O}_8^{-2}]^{1/2}[\text{M}]^{3/2} \quad (11)$$

The order of reaction with respect to the monomer from 1.5 to 1 would be described by the previous equation. However, it is crucial to mention that for monomolecular termination involving the reaction between the propagating radical and a fragment of persulfate, the order of reaction would reach 2.[18]

If R_{pm} represents polymerization rate by monomolecular termination [Eq. (12)] and

$$\alpha = \frac{k_{tb}}{k_{tb} + k_{tm}}$$

in which α is the ratio of monomolecular termination constant to summation of mono and biomolecular termination constants. Where k_{tb} and k_{tm} represent the bimolecular and monomolecular termination constants, respectively:

$$R_{pm} = k_p \left(\frac{K_c}{1 + K_c}\right) \frac{2k_3}{k_{tb}} [\text{M}] \quad (12)$$

Then, R_p could be adjusted to Eq. (13):

$$R_p = \omega [\text{S}_2\text{O}_8^{-2}]^{1/2}[\text{M}]^2 \left\{ \alpha \frac{1}{k_{tm}} \left(\frac{K_c}{1 + K_c[\text{M}]} \frac{2k_3}{[\text{S}_2\text{O}_8^{-2}]}\right)^{1/2} \right.$$
$$\left. + \left(\beta \left(\frac{1}{k_{tb}[\text{M}]}\right)^{1/2}\right)\right\} \quad (13)$$

ω are defined for simplicity of above reaction, where

$$\omega = (2k_3)^{1/2} k_p \left(\frac{K_c}{1 + K_c[\text{M}]}\right)^{1/2}$$

and

$$\beta = 1 - \alpha$$

Here, when the monomer and initiator concentrations and also the initiation type are considered, the power dependence of the polymerization rate on the monomer would change up to 2.

In complex theory, E_a is predicted to be greater than that which matches cage effect theory. There is nothing known with which to compare the aqueous polymerization of AMPS E_a. The overall E_a for most polymerizations initiated by thermal decomposition is about 80–90 kJ/mol. On the other hand, the reported E_a values of acrylamide were about 70 and 48 kJ/mol.[1] The high level of overall E_a in this study could be in a good agreement with complex theory.

CONCLUSIONS

The ^{1}H-NMR technique is one of the most practical and precise methods for kinetic understanding of free-radical polymerization. The aqueous radical polymerization of AMPS in the presence of a thermal initiator (KPS) was studied. The obtained data led to the determination of the order of reaction based on the monomer and initiator. The calculated amounts were $n = 1.94$ and $p = 0.49$ with excellent deviations.

The overall rate of the AMPS polymerization reaction at the desired monomer and initiator concentrations are given as follows:

$$R_p = k[\text{M}]^{1.94}[\text{I}]^{0.49}$$

The dependence of the polymerization rate on the monomer concentration was in a good agreement with complex theory, and a power of 0.49 for the initiator concentration was consistent with classical kinetic theory.

Also, E_a and k_0 over the range 35–47°C were determined to be 92.7 kJ mol^{-1} K^{-1} and 3.385×10^{13} mol L^{-1} s^{-1}, respectively.

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