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ORIGINAL PAPER

Kinetic study of 2-acrylamido-2-methylpropanesulfonic acid in free-radical polymerization method by differential scanning calorimetry

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Abstract Aqueous free-radical polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) in the presence of potassium persulfate (KPS) as thermal initiator was studied by differential scanning calorimetry (DSC). Effect of temperature, monomer, and initiator concentration on polymerization rate was studied. Obtained recorded data represented order of reaction with respect to monomer greater than unity (1.56). Among the theories presented order of reaction more than one, the gage effect theory in the range of monomer concentration (0.966–2.410 mol/L) had a good agreement with mechanism of AMPS polymerization. The order with respect to KPS was 0.52 which was consistent with classical kinetic theory. Calculated amount of activation energy in overall rate of reaction was 83 kJ/mol K.

Keywords DSC · AMPS · Thermal initiator · Kinetic study · Free-radical polymerization

Introduction

In recent years, water soluble polymers have been attracted a great attention by environmental scientist. Polymerization in aqueous media was developed for elimination of ecologically hazardous organic solvents [1]. poly (AMPS), and its derivatives are often used as water-soluble polymers with various applications. These polymers are extensively used in a extensive range of industrial products and processes such as, food, cosmetics, paints pigments, thickeners, coatings, personal care products, adhesives, inks, etc. [2]. Most of these polymers are produced by free-radical polymerization because of its advantages such as simplicity and versatility [3].

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Obtaining high molecular weight polymer, uniform crosslinker incorporation, low residual monomer levels, and high production rates requires a detailed and precise knowledge of polymerization kinetics [4]. Hence, according to the industrial application of poly AMPS, optimization of polymerization process and control characteristics of final product is essential.

A driving force for polymerization reaction is the heat of polymerization which governs the rates and kinetics of polymerization. So, accurate measurement of thermochemical data is an appropriate method for following the kinetic of polymerization. Thus, differential scanning calorimetry (DSC) is a suitable technique for recording heat production of chemical process because of its advantages such as small sample size which help better temperature control, handiness of manipulation, performance rapidity, and versatility [5]. Most of kinetic studies by using DSC method, the reaction has been initiated by UV or high-energy radiation such as X or γ-rays in solid state polymerization [6–9]. Owing to the industrial importance of poly AMPS among water-soluble polymers, its kinetic understanding is essential in order to predict polymerization rate, molecular weight or other essential parameters during the polymerization process. Thus, in this study, aqueous kinetic of AMPS polymerization initiated by a thermal initiator was studied by using DSC. Order of reaction of each component in the corresponding rate equation was determined. Activation energy was calculated for aqueous polymerization of AMPS, besides. Derived kinetic parameters were used for polymerization process kinetic understanding.

Experimental

Materials

AMPS and potassium persulfate (KPS) were purchased from Fluka and Merck, respectively, and were recrystallized from ethanol for further purification.

DSC studies

In this study, DSC thermograms were obtained on a NETSCH DSC 200 F3 instrument. Monomer and initiator were weighted precisely and dissolved in deionized water. Concentrations used for AMPS and KPS are presented in Table 1. Closed pans were loaded with 22–24 mg of the solution. In order to prevent side and retarding reactions, a hole was produced in pans and all the reactions were carried out under the nitrogen atmosphere.

Results and discussions

DSC thermograms at isothermal conditions were presented in Table 1. In order to sure complete reaction of entire monomer for all samples a non-isothermal run, from ambient temperature to 80 °C at heating rate of 1 °C/min, was purposed.

Table 1 Formulation used for kinetic study of AMPS aqueous polymerization

Samples	[AMPS]0 (mol/L)	[KPS]0 (mol/L)	Isothermal temperature (°C)
1	0.966	0.074	40
2	0.966	0.148	40
3	0.966	0.185	40
4	1.966	0.074	40
5	2.410	0.074	40
6	1.450	0.148	35
7	1.450	0.148	40
8	1.450	0.148	47

Absence of exothermic peak for the samples demonstrated complete conversion of monomer in isothermal run.

DSC kinetic analysis at different initiator concentrations

Monomer molar concentration was kept constant and solutions with various amount of initiator were prepared. Samples number 1–3 from Table 1 were used in these series of experiments. DSC thermogram of polymerization for samples 1–3 are illustrated in Fig. 1.

Monomer conversion was calculated as a fraction of exothermic heat in a specific time to total exothermic heat of polymerization Fig. 2 shows a typical calculation of monomer conversion (π) at 7 min in which A_p and A are peak area at 7 min and total peak area of polymerization, respectively. Variation of conversion versus time is plotted in Fig. 3. Induction time would be decreased by increasing initiator in polymerization system because of increasing polymerization rate.

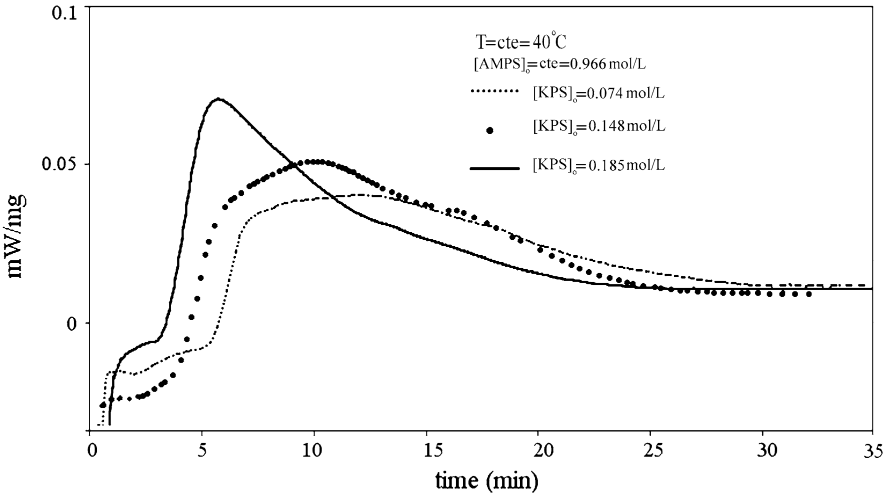

Fig. 1 DSC thermogram of polymerization at different initiator content

Following equation was used to evaluate order of reaction [1].

$$R_{\mathrm{p}} = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = \frac{\mathrm{d}\pi}{\mathrm{d}t}[M_0] = k[M]^n[I]^p \tag{1}$$

where π, R_{p}, $[I]$, $[M]$, and $[M_0]$ are monomer conversion, polymerization rate, initiator, and monomer concentrations, and initial concentration of monomer, respectively.

In constant initial monomer concentration, slope of $-\ln R_{\mathrm{p}}$ versus $-\ln[I]$ reveals the order of reaction with respect to the initiator concentration (all the calculations were carried out at 5% monomer conversion). Corresponding to Fig. 4, calculated amount of p was 0.52 which was in a good agreement with classical kinetic theory of radical polymerization. In classical kinetic theory, order of reaction with respect to initiator depends on the square root of initiator concentration [1].

DSC kinetic analysis at different monomer concentrations

Exothermic peak of solutions with different monomer molar concentrations and a constant amount of initiator (samples 1, 4, and 5 from Table 1) were obtained. Variations of conversion versus time are plotted in Fig. 5. Conversion variation is shown in Fig. 6. Determined n value by slope of $-\ln R_{\mathrm{p}}$ versus $-\ln[M]$ plot was 1.56 (Fig. 7).

So, the overall rate of AMPS aqueous polymerization is described by Eq. 2;

$$R_{\mathrm{p}} = k[M]^{1.56}[I]^{0.52} \tag{2}$$

Determination of k_0 and activation energy

If E_{a} is representative of overall activation energy, general rate of polymerization is given by Eq. 3;

$$R_{\mathrm{p}} = k_0 e^{-\frac{E_{\mathrm{a}}}{R}\frac{1}{T}}[M]^n[I]^p \quad \text{or} \quad \ln R_{\mathrm{p}} = \ln(k_0[M]^n[I]^p) - \left(\frac{E_{\mathrm{a}}}{R}\right)\frac{1}{T} \tag{3}$$

DSC thermogram of samples 6, 7, and 8 is shown in Fig. 8 Variation of reaction rate by temperature is shown in Fig. 9. E_{a} and k_0 could be deliberated from slope

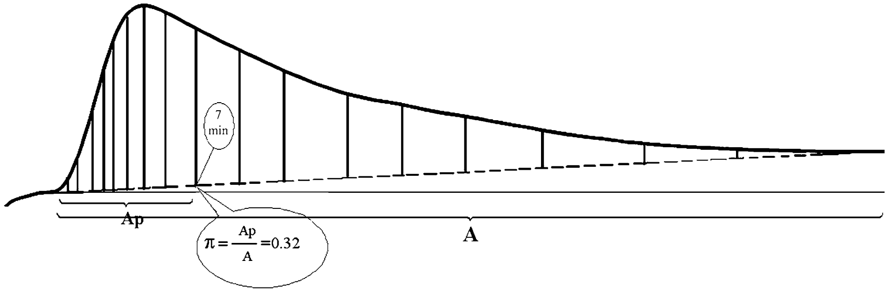

Fig. 2 Partial area of exothermic peak of sample 3 from Table 1 at 7 min

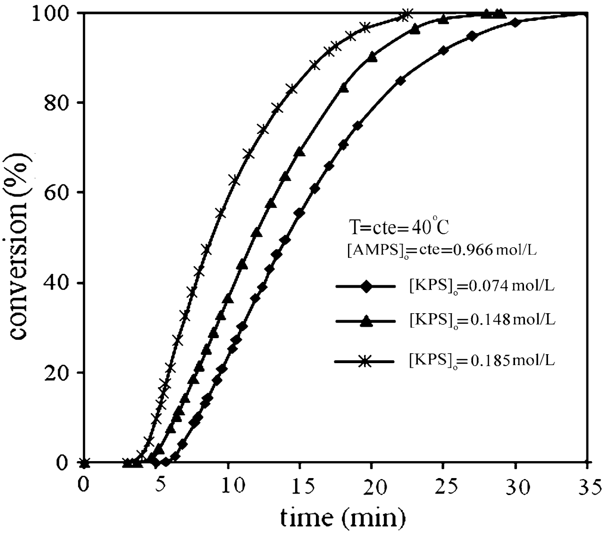

Fig. 3 Monomer conversion versus time at different initiator content

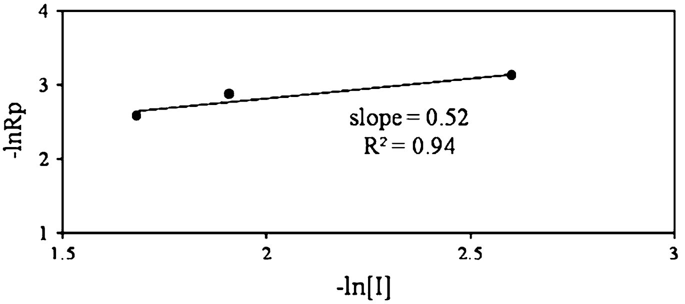

Fig. 4 Variation of $-\ln R_p$ versus $-\ln [I]$

and intercept of $-\ln R_p$ versus $1/T$ plot (Fig. 10) in a constant amount of monomer and initiator. E_a was 83 kJ/mol K k_0 determined by intercept of mentioned plot was 1.2×10^{13} mol L^{-1} s^{-1} which was about the same amount that obtained from intercept of Figs. 3 and 6.

Mechanistic study

Dependence of polymerization rate on monomer concentration greater than unity can be described by three theories: (a) the solvent transfer theory, (b) the cage effect theory, and (c) the complex theory [1, 10].

The solvent transfer theory was ignored in aqueous polymerization of AMPS because derived sulfur-containing fragment from persulfate are very reactive toward monomers and no data is available for formation of hydroxyl-free radical in water [10].

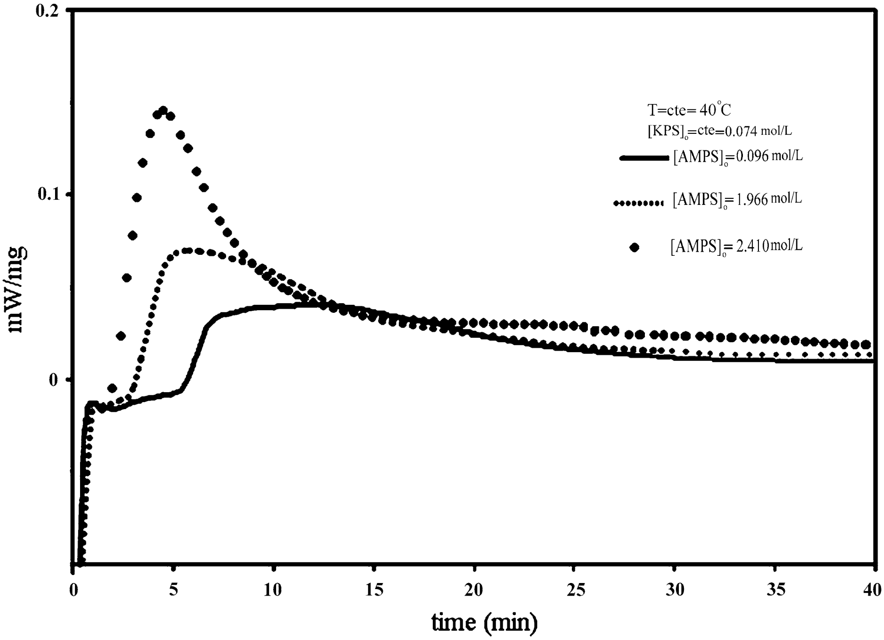

Fig. 5 DSC thermogram of polymerization at different monomer content

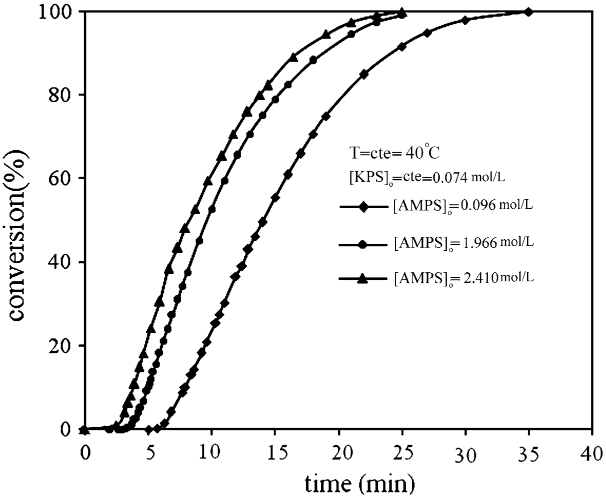

Fig. 6 Monomer conversion versus time at different monomer content

Cage effect theory is based on forming a barrier for separation of sulfur-containing fragment from the surrounding solvent molecules. If the parentheses demonstrate fragments in a solvent cage, the following mechanisms are expected;

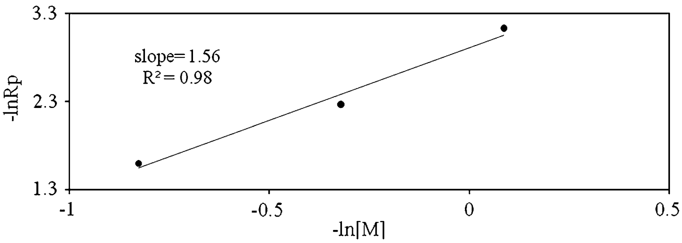

Fig. 7 Variation of ln R_p versus −ln $[M]$

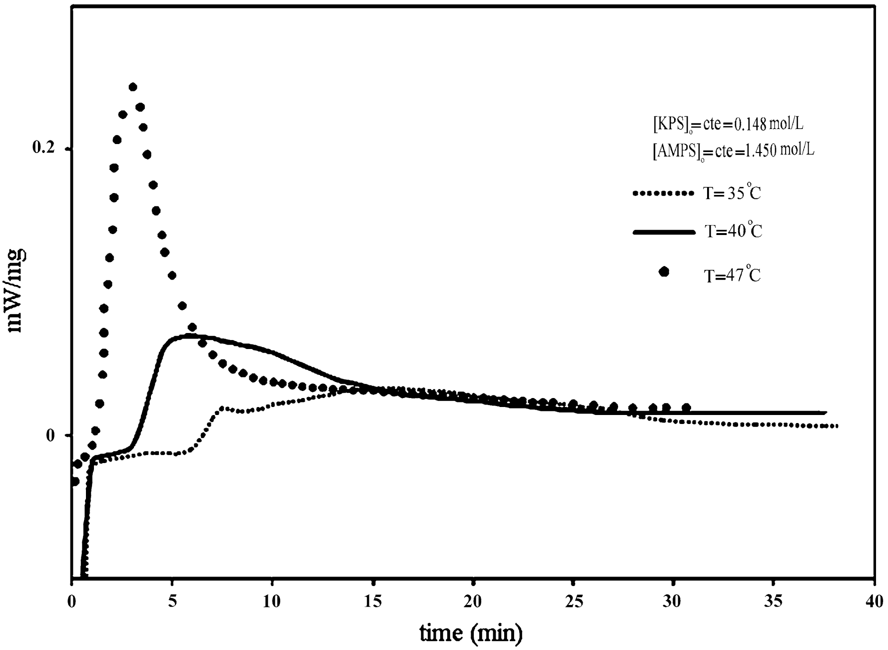

Fig. 8 DSC thermogram of polymerization at different temperatures

$$S_2O_8^{-2} \xrightarrow{k_1} 2SO_4^{-\bullet} \tag{4a}$$

$$SO_4^{-\bullet} + M \xrightarrow{k_{i1}} M^{\bullet} \tag{4b}$$

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet} \tag{4c}$$

$$M_g^{\bullet} + M_k^{\bullet} \xrightarrow{k_t} P_{g+k} \tag{4d}$$

$$S_2O_8^{-2} \xrightarrow{k_4} (2SO_4^{-\bullet}) \tag{4e}$$

$$(2SO_4^{\bullet}) \xrightarrow{k_5} S_2O_8^{-2} \tag{4f}$$

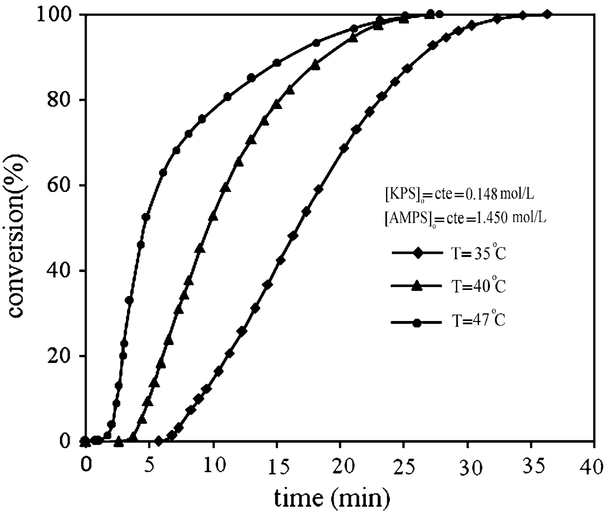

Fig. 9 Monomer conversion versus time at different temperature

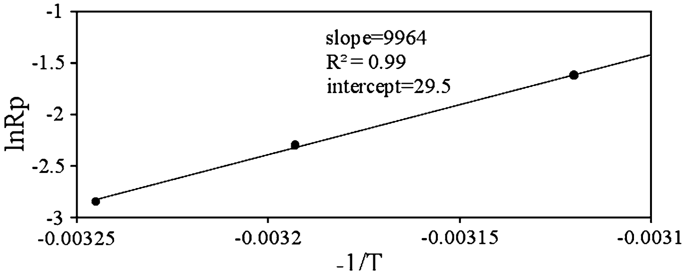

Fig. 10 Variation of ln R_p versus $-1/T$

$$(\mathrm{SO}_4^{-\bullet}) + M \xrightarrow{k_6} M^\bullet \tag{4g}$$

$$(\mathrm{SO}_4^{-\bullet}) + \mathrm{H_2O} \xrightarrow{k_7} \mathrm{HSO}_4^- + {}^\bullet\mathrm{OH} \tag{4h}$$

$$(\mathrm{SO}_4^{-\bullet}) \xrightarrow{k_8} \mathrm{SO}_4^{-\bullet} \tag{4i}$$

$$2\mathrm{SO}_4^{-\bullet} \xrightarrow{k_9} \mathrm{S_2O_8^{-2}} \tag{4j}$$

By considering some assumptions, polymerization rate could be described by Eq. 5;

$$R_\mathrm{p} = k_\mathrm{p}\left(\frac{2k_1}{k_t}\right)^{1/2}[\mathrm{S_2O_8^{-2}}]^{1/2}\left(\frac{k_6[M]+k_7+k_8}{k_6[M]+k_7+k_8+k_5}\right)^{1/2}[M] \tag{5}$$

Order of reaction corresponding to monomer concentration depends on two competitive terms ($k_6[M]$ and $k_7 + k_8$). In the case that $k_7 + k_8 \geq k_6\,[M]$, the rate is first order base on monomer. On the other hand, if $k_7 + k_8 \leq k_6\ [M]$, monomer dependency varies from power of 1–1.5.

Then, with respect to conditions such as monomer concentration (0.966–2.410 mol/L) cage effect theory could predict the dependency of polymerization rate on monomer concentration up to 1.5 [11].

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

$$\mathrm{S_2O_8^{-2}} + M \overset{K_\mathrm{c}}{\leftrightarrow} \mathrm{S_2O_8^{-2}} - M \tag{6a}$$

$$\mathrm{S_2O_8} - M^{-2} \xrightarrow{k_3} M^{\bullet} + \mathrm{SO_4^{-\bullet}} \tag{6b}$$

Complex concentration is given by Eq. 7;

$$[\mathrm{S_2O_8} - M^{-2}] = K_\mathrm{c}[\mathrm{S_2O_8^{-2}}][M]/(1 + K_\mathrm{c}[M]) \tag{7}$$

The general rate of polymerization, with respect to usual assumption, is given by Eq. 8;

$$R_\mathrm{p} = k_\mathrm{p}\left(\frac{2k_3}{k_t}\right)^{1/2}\left(\frac{K_\mathrm{c}}{1 + K_\mathrm{c}[M]}\right)^{1/2}[\mathrm{S_2O_8^{-2}}]^{1/2}[M]^{3/2} \tag{8}$$

Order of reaction with respect to monomer from 1 to 1.5 would be described by above equation.

In cage effect theory, activation energy is predicted to be smaller than that matches complex theory. There is nothing known for aqueous polymerization of AMPS activation energy to be compared with. However, activation energy that was measured in this study was in the range of conventional activation energy of radical polymerization (80–90 kJ/mol K) [12]. Thus, in monomer concentration ranges from 0.966 to 2.410 mol/L and temperature ranges 35–47 °C polymerization mechanism of AMPS in aqueous medium could be described by the cage effect theory.

Conclusion

Aqueous radical polymerization of AMPS in the presence of a thermal initiator (KPS) was studied by DSC. Obtained exothermic peaks were led to determine conversion versus time and then order of reaction based on monomer and initiator. Calculated amount resulted $n = 1.56$ and $p = 0.52$. Then, overall rate of AMPS polymerization reaction for monomer concentration ranges from 0.966 to 2.410 mol/L are given as bellow:

$$R_\mathrm{p} = k[M]^{1.56}[I]^{0.52}$$

Activation energy of AMPS polymerization at the given condition was 83kJ/mol K n value and activation energy supported the assumption that polymerization kinetic was according to cage effect theory.

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