Kinetics of Acrylamide Solution Polymerization Using Potassium Persulfate as an Initiator by *in situ* IR

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Abstract: We have studied the polymerization kinetics of acrylamide in aqueous solution with potassium persulfate as an initiator by using quantitative real-time *in situ* IR spectroscopy and monitoring the profiles of peaks in the range 1900-850 cm^{-1}. The conversion of acrylamide was calculated from the disappearance of the peak at 988 cm^{-1}, which is the out-of-plane bending mode of the =C-H unit, normalized to the C=O stretching peak at 1675 cm^{-1} as an internal standard. For reaction temperatures in the range 40-65 °C and initiator and monomer concentrations of 0.9-2.6 mmol/L and 0.5-1.1 mol/L, respectively, we deduced that the rate of monomer consumption follows the relation $R_p = k[K_2S_2O_8]^{0.5}[M]^{1.35\pm0.10}$. In addition, we obtained activation parameters from an evaluation of the kinetic data.

Keywords: acrylamide, potassium persulfate, kinetics, *in situ* IR spectroscopy.

Introduction

In recent years, water-soluble polymer is getting more important because of the restriction in environmental and industrial areas for the organic solvents which are the main source of air pollution. Polyacrylamide is one of the water-soluble polymers which was widely applied within the fields, such as water modification, paper treatments, textile applications, adhesives, surface coatings, hair spray, etc.[1]

The previous researchers[2-7] made a series of comprehensive studies in the reaction mechanism for the polymerization for acrylamide in water. Riggs[2] was the first to use potassium persulfate as an initiator to this polymerization and analysis of the kinetic data by the dilatometer technique. Lin[3] used the gravimetry technique to determine the dependence of initiator and monomer concentration during polymerization. However, the dilatometry and gravimetry methods have a response time too long to follow *in situ* the polymerization kinetics. Alternatively, samples can be withdrawn from the reactor and analyzed for residual monomer in solution at various times by spectroscopic or chromatographic techniques. Sample removal techniques can be very difficult, especially since many reactions are extremely sensitive to oxygen and other impurities that can be introduced during

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sampling. *In situ* mid-IR spectroscopy is a real-time monitoring technique that is well suited to obtain real-time structural and kinetic information of controlled polymerization process such as stable free radical polymerization.[8] Previously, Long *et al.* have utilized *in situ* near-infrared (10000~4000 cm^{-1}) spectroscopy using fiber optics probe technology to obtain solution polymerization kinetics of living anionic processes.[9] More recently, the first mid-IR Attenuated Total Reflection (ATR) fiber optics monitoring of carbocationic polymerization of isobutylene and styrene were reported by Puskas *et al.*[10] At the same time, Storey *et al.* reported the mid-IR monitoring of carbocationic polymerization using an ATR technique based on conduit technology.[11] Other groups are also actively pursuing this powerful technology to monitor various polymerization processes.[12] Real-time FTIR monitoring is become an increasingly popular tool to monitor polymerization reaction.

In this paper, using the *in-situ* IR spectroscopy employing a ReactIR 1000, the polymerization kinetics of acrylamide in aqueous solution with potassium persulfate as an initiator was studied. The ReactIR has sufficient sensitivity and aquisition speed to detect intensity changes of specified wave numbers for the reactants and/or products during the polymerization without any sampling procedure. In order to investigate the kinetic behaviors, we analyze the rate of polymerization by monitoring the disappearance of the out-of-plane bending mode of =C-H, which was interpreted

using the experimental spectra in terms of the ones calculated at B3LYP/6-31G(d) level.

Experimental

Chemicals. Acrylamide (electrophoresis grade) and potassium persulfate (analytical grade, 99.99%) were purchased from Aldrich Chemical. Acrylamide was twice recrystallized from chloroform and dried under vacuum at room temperature. Potassium persulfate was used without further purification. Water was filtered and deionized in an ultrapure water system.

In situ **IR.** FT-IR spectra were monitored via real-time *in-situ* by ReactIR™ 1000 analysis system (ASI Applied Systems, Millersville, MD) which was equipped with a MCT (Mercury Cadmium Telluride) detector and DiComp (Diamond Composition) insertion probe with diamond wafer as a multiple reflection ATR (Attenuated Total Reflection) element. In this investigation, each spectrum was the Fourier transformation of 256 acquisitions collected over the spectral ranges 1900~850 cm^{-1} with a time period of 2 min and instrument resolution of 4 cm^{-1}.

Polymerization. Polymerizations were carried out under dry nitrogen atmosphere in a 300 mL four-neck round-bottom flask that included DiComp probe, impeller, condenser, and thermocouple probe with dry nitrogen purge. Acrylamide dissolved in water was introduced into the reactor in the water bath at the desired reaction temperature. The reaction mixtures were stirred at a constant rate (200 rpm) with a mechanical stirrer, and its temperature was monitored during the polymerization. After the temperature reached the desired value, the polymerization was initiated by adding the initiator into the system.

Results and Discussion

The polymerization was run in the water as a solvent, the solvent spectrum of pure water was initially collected at the reaction temperature, and the reaction mixtures spectra were obtained via solvent spectrum subtraction. Figure 1 shows the spectra acquired every 2 min over the entire reaction time (150 min). The intensities of some peaks, caused by one or more functional groups, were changed as the reaction proceeded. The theoretical vibration spectra of both acrylamide and polyacrylamide were interpreted by using GRAMS/32 software from Galactic Industries Corporation.

Full optimization of the studied molecules was performed at B3LYP level combined with the 6-31G(d) basic set. The stretching mode of C=O (1675 cm^{-1} peak), the stretching mode of C=C (1590 cm^{-1}), the bending mode of =C-H (1436 cm^{-1}), the bending mode of -C-H$_2$ (1328 cm^{-1}), and the out-of plane bending mode of =C-H (988 cm^{-1}) were assigned on the basis of the calculated results of each normal mode and the observed spectra. All calculations were per-
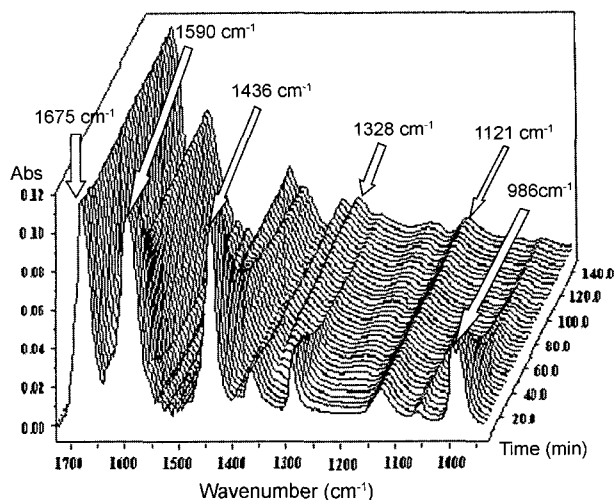

Figure 1. Time dependency of *in situ* FT-IR spectra during the polymerization at initiator concentration 2.25 mmol/L, monomer concentration 0.9 mol/L and temperature 50 °C.
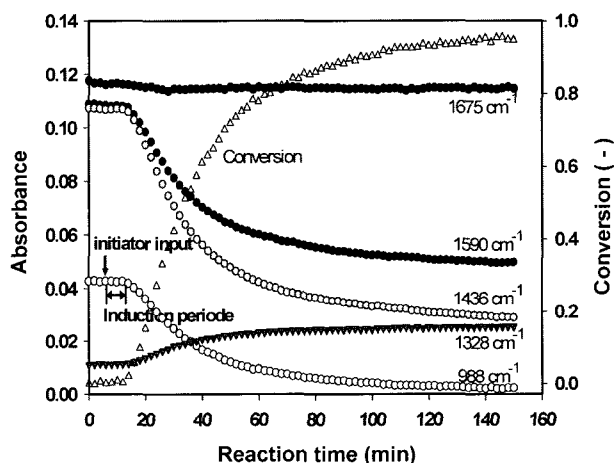

Figure 2. Real time profiles of C=O stretching peak (1675 cm^{-1}), C=C stretching (1590 cm^{-1}), =C-H bending (1436 cm^{-1}), -C-H bending (1328 cm^{-1}) and =C-H out-of-plane bending (988 cm^{-1}), and the conversion calculated from =C-H out-of-plane bending peak for the entire reaction period.

formed by using Gaussview molecular visualization program and Gaussian98 program package on a personal computer. Figure 2 shows the profiles as mentioned above and the conversion was calculated from 988 cm^{-1} peak for the entire reaction period by *in situ* IR spectroscopy.

The polymerization was not started immediately but some time later, which is the so called induction period. In all monitored polymerizations, the induction period was observed without reproducibility, and it was not related to the initial monomer and initiator concentrations and reaction temperatures. Many authors have reported a lack of repro-

ducibility in the similar experiments,[13-15] even when the different experimental techniques were employed. They concluded that the inhibition period was caused by traces of residual oxygen left after degassing. Since our degassing system employed in the polymerization is not perfect, we did not study it further. The intensities of 1590, 1436 and 988 cm^{-1} peaks were weakened steadily. Among these peaks, the 1590 and 1436 cm^{-1} peaks were overlapped with other peaks, but 988 cm^{-1} peak was not overlapped. Therefore, the 988 cm^{-1} peak was used to calculate the conversion of the monomer. The peak height at 988 cm^{-1} and the partial area under this peak (1040~932 cm^{-1}) were examined, but no deviations are observed as in Storey's results.[11] In order to correct the sample-to-sample fluctuations in the spectra, these real-time displays are updated by the linear baseline between 1725 and 928 cm^{-1} with successive spectrum that are acquired.

Figure 3 shows the profiles of 988 cm^{-1} peak obtained in which the initial monomer concentrations were varied to 0.5~1.1 mol/L at initiator concentration of 2.25 mmol/L and reaction temperature of 50 °C. The consumption rate of monomer was increased as the initial monomer concentration is increased. In radical polymerization reactions, the empirical monomer consumption rate is expressed as;

$$R_p = -d[M]/dt = k[I_2]^a[M]^b \qquad (1)$$

Assuming quasi-steady-state approximation (QSSA), the concentration of initiator is not varied, Eq. (1) was represented as follows;

$$R_p = -d[M]/dt = k_1[M]^b, where \quad k_1 = k[I_2]^a \qquad (2)$$

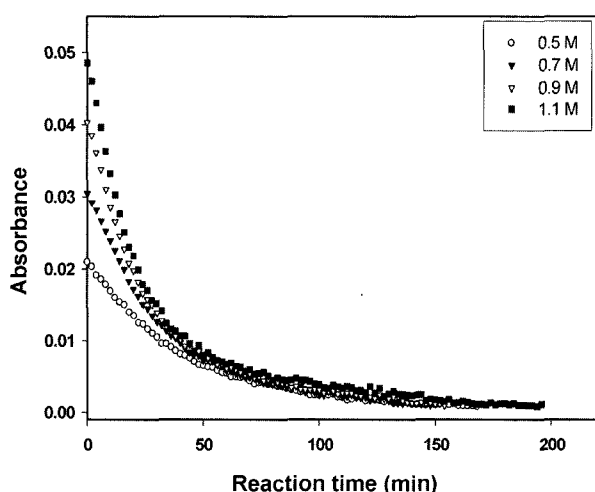In this work, the reaction order with respect to the mono-

Figure 3. Real time profiles of the out-of-plane bending 988 cm^{-1} peak during the polymerization at 50 °C, initiator concentration 2.25 mmol/L, and various initial monomer concentrations.

mer consumption was determined by non-linear least-square regression to minimize the sum of the residuals using FMINSEARCH and ODE45 procedures in Matlab 6.5.

$$Min\sum_{i=j}^{j+n}[M_{i,exp} -M_{i,cal}]^2 \quad for \quad j = 1, \cdots, 20 \qquad (3)$$

where, $n = 10$ which is the number of observation for the 20 min, j is the initial conditions of differential Eq. (2), $M_{i,exp}$ and $M_{i,cal}$ are the measured and predicted monomer concentrations. For the initial monomer concentrations of 0.5, 0.7, 0.9, and 1.1 mol/L, the calculated reaction order was obtained to 1.12, 1.16, 1.31, and 1.35 from the beginning of reaction to 10 min respectively, and it approached to the constant values 1.25 1,32, 1.38, and 1.45 after then. From these results, the reaction order with respect to the monomer consumption was shown as 1.23±0.12 initially and 1.35± 0.10 sometime later. These were similar to Riggs[2] (1.25) and Hunkeler[4] (1.34±0.12), but different from Collinson[16,17] (1.0). Riggs results were obtained at 30 °C and with monomer concentrations between 0.05 and 0.94 mol/L, initiator between 0.9 and 52.1 mmol/L, and he drove the rate of monomer consumption from cage effect, complex theory and solvent-transfer theory, the dependence on monomer concentration varied from a power of 1.5 to 1.0 as the concentration increases. But Hunkeler results were obtained at 50 °C with monomer concentrations between 3.35 and 6.70 mol/L, initiator 0.25 mmol/L of the aqueous phase, varied in 5% increments. He proposed the hybrid mechanism, in which the overall polymerization rate order with respect to monomer concentration lies between 1.0 and 1.5, governed by the strength of the initiator-monomer association. In our experiments, the reaction order was initially increased with respect to the increase of initial monomer concentration, and it was increased as the polymerization proceeded. In the earlier step of polymerization, the reaction rate is getting faster at high initial concentration of monomer, because more radicals, which were produced by the initiator, get wrapped in the solvent-monomer solution. As the reaction proceeded, the reaction order with respect to monomer concentration was increased with the monomer concentration decrease, which can be explained by the cage effect theory such that the reaction between caged radicals and monomer molecules in the cage wall were dominant.

In order to calculate the dependence of initial initiator concentration on monomer consumption rate, the conversion of monomers were calculated as shown in Figure 4, where the initial initiator concentration varied between 0.90, 1.35, 2.25 and 2.60 mmol/L at 50 °C and initial monomer concentration 0.7 mol/L. Under these conditions, because of the reaction order with respect to monomer concentration was not unity, the integral forms of Eq. (1) denoted to the monomer conversion x,

$$(1-x)^{1-b}-1 = k_2t = k[I_2]^a[M_0]^{b-1}(b-1)t \qquad (4)$$

where the conversion $(x = 1 - [A_t \cdot A_{ref,0}]/[A_0 \cdot A_{ref,t}])$ is calculated from the initial peak of 988 cm^{-1} of monomer and reference peaks, A_0 and $A_{ref,0}$, respectively, and their corresponding values at time t, A_t and $A_{ref,t}$ as by Mijovic[18] or Kang.[19] Various reference peaks were examined and the most reproducible results were obtained using the peak due to the carbonyl C=O stretching vibration of the monomer at 1675 cm^{-1} peak. The left hand side of Eq. (4) is plotted as a function of reaction time (not shown), and the logarithm of observed slopes were plotted as the function of logarithm of initial initiator concentrations as shown in Figure 5. The order with respect to the initiator concentration on polymerization was found to be 0.517, which clearly indicates that termination occurs through bimolecular interaction of growing polymer chain radicals.[20-23] It was consistent with the classic kinetic
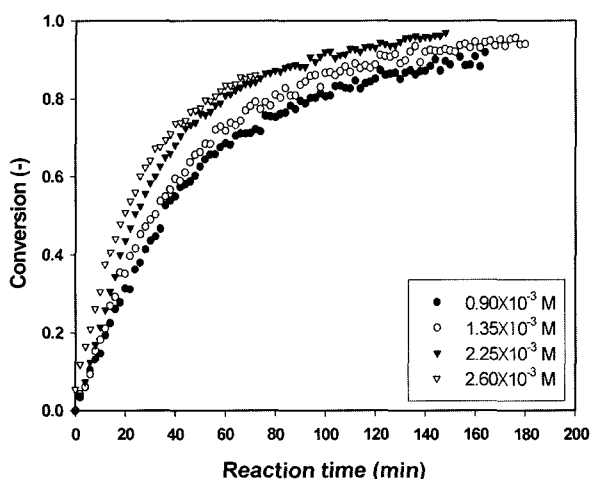
theory, which predicts that the polymerization rate is proportional to the square root of the initiator concentration, as also indicated by most of the previous researchers.[2,18,24-27] Therefore, the overall monomer consumption rate is expressed as;

$$R_p = -d[M]/dt = k[I_2]^{0.5}[M]^{1.35 \pm 0.10}$$
(5)

Figure 6 shown the conversions of monomer for various reaction temperatures 40~65 °C at monomer concentration 0.7 mol/L and initiator concentration 2.25 mmol/L. The rate constants in Table I were calculated from data below 80% conversion using Eq. (4). The data in Table I were used to determine Arrhenius behaviour and activation properties of polymerization. The Arrhenius plot of $\ln(k_2)$ versus $1/T$ in Figure 7 gives a good linearity and activation energy of 67.2 kJ/mol or 16.1 kcal/mol. These values agree with Riggs results (16.9 kcal/mol).[2] The activation enthalpy and entropy which were calculated using Eyring equation are 65.5 kJ/mol and -79.2 J/mol·K.

Figure 4. Time-conversion curves for various initial initiator concentrations at 50 °C and monomer concentration 0.7 mol/L.

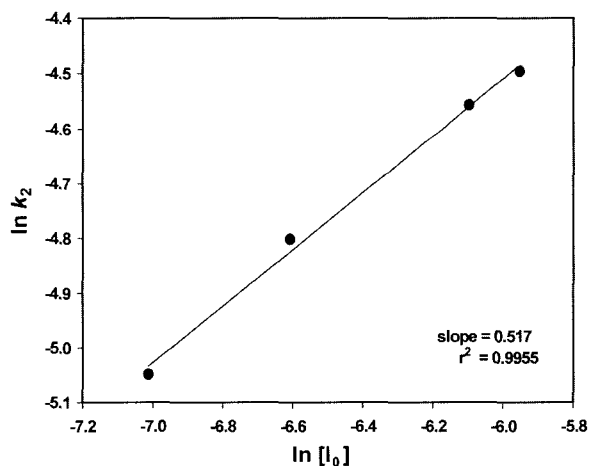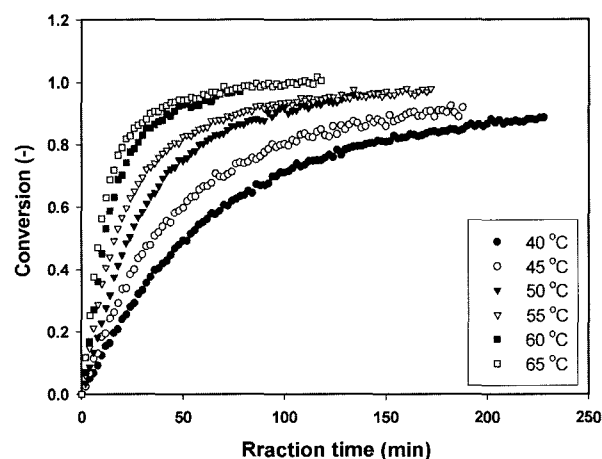Figure 6. Time-conversion curves for various reaction temperatures at monomer concentration 0.7 mol/L and initiator concentration 2.25 mmol/L.

Figure 5. Plot of $\ln k_2$ vs. $\ln[I_0]$ to determine the order of initiator concentration.

Table I. Polymerization Temperature and Corresponding Kinetic Parameters for Acrylamide

Temperature (°C)	Rate Constant k_2 (min^{-1}) $\times$ 10^3	R^2	80% Conversion Time (min)
40	4.3123	0.9963	140
45	5.8482	0.9896	100
50	10.5936	0.9942	60
55	12.5988	0.9969	44
60	22.6610	0.9864	28
65	26.6692	0.9901	20

E_a = 67.2 kJ/mol
r^2 = 0.9877

ln k_2

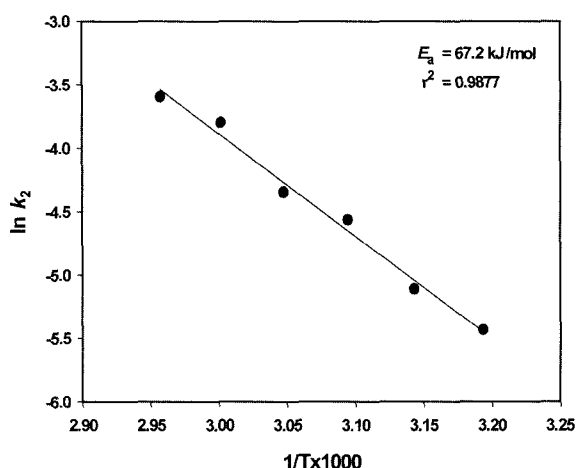2.90 2.95 3.00 3.05 3.10 3.15 3.20 3.25

1/Tx1000

Figure 7. The Arrhenius plot of lnk_2 vs. 1/T.

Conclusions

Polymerization of acrylamide was carried out in aqueous solution with potassium persulfate as an initiator by real-time *in-situ* FT-IR spectroscopy, to investigate the effects of polymerization temperatures and concentrations of initiator and monomer, on the reaction order with respect to monomer consumption. Important results are as follows.

1. It was found that the peak at 988 cm^{-1} was the out-of-plane bending of =C-H from the observed spectra and calculated results by Gaussview and Gaussian98. The conversion of monomer was calculated from the disappearance of 988 cm^{-1} peak normalized to the 1675 cm^{-1} as an internal standard.

2. In the range of monomer concentration 0.5~1.1 mol/L, the reaction order of monomer concentration on monomer consumption was expressed as 1.23±0.12 initially, and 1.35 ± 0.10 sometime later.

3. In the range of initiator concentration 0.90~2.60 mmol/L, the reaction order of initiator concentration on monomer consumption was expressed as 0.5. Therefore, overall consumption rate of monomer was estimated as follows;

$$R_p = k[K_2S_2O_8]^{0.5}[M]^{1.35 \pm 0.10}$$

4. The activation energy(E_a), enthalpy($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) were found to be 67.2, 65.5 kJ/mol and -79.2 J/mol·K for the present polymerization system.

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