Kinetic Study of Acrylic Acid Solution Polymerization

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The kinetics of acrylic acid (AA) solution polymerizations were characterized under various polymerization conditions using differential scanning calorimetry. The AA polymerization rate R_p decreased with increasing pH over all pH values due to the decreased reactivity of ionized AA relative to the unionized monomer. The rate behavior above pH 6 was suggestive of diffusion-controlled termination kinetics. The degree of ionization thus impacted not only the reactivity of species in solution but also the diffusive characteristics of propagating macroradicals. As the AA concentration was increased, the change in polymerization rate with pH was substantially less. The temperature dependence of R_p indicated that the overall activation energy for polymerization varied with temperature, due to diffusion-controlled termination kinetics. The polymerization rate was significantly higher when a multifunctional cross-linking agent was added, because of the gel effect, even while maintaining a constant double bond concentration.

Introduction

Polyelectrolytic polymeric systems possess properties useful in a wide range of applications. Polyelectrolytes are used in the formulation of membranes, biomaterials, flocculants, and sedimentation products. Additionally, they are used as superabsorbent materials in products such as diapers, feminine hygiene products, adult incontinence products, communications cable, agricultural products, construction materials, and food packaging (Buchholz, 1990; Zhao et al., 1995). As applications for synthetic polyelectrolytes grow in number, the study of polymerization reactions involving ionizable monomers becomes increasingly important.

Cross-linked poly(sodium acrylate) is the most common superabsorbent polymer. It is capable of absorbing up to 30 times its own weight of urine or other electrolyte solution. The gel product is manufactured by free radical initiated copolymerization of acrylic acid (AA) with a small amount of a multifunctional cross-linking agent. Neutralization is carried out by addition of base, usually an alkali metal hydroxide, either before or after the polymerization. Although both solution polymerization and suspension polymerization are commonly employed (Buchholz, 1994), the present work was concerned solely with the solution polymerization of AA in water.

Buchholz (1990, 1994) and Zhao et al. (1995) have noted that the exact conditions of polymer synthesis and the kinetics of the polymerization reaction determine the AA network structure, which in turn dictates the material properties. For this reason, a thorough understanding of the kinetics of AA polymerizations under industrially relevant reaction conditions is most important.

The kinetics of the AA reaction system are quite complicated, since except at extremely high or extremely low pH, the AA monomer exists in both the unionized acid form and in the ionized metal salt form. Thus, AA polymerization, even in the absence of a cross-linking monomer, is a copolymerization, with comonomers acrylic acid and metal acrylate. The relative concentrations of the comonomers at a given pH (extent of neutralization) are described by the Henderson-Hasselbach equation, which relates the fractional ionization α for a component of known pK_a to the solution pH

$$\mathrm{pH} \cong pK_a + \log \frac{\alpha}{1-\alpha}$$

AA has a pK_a value of 4.20, while poly(acrylic acid) (PAA) has a pK_a of 4.75 (Nemec and Bauer, 1988). The equation can also be used to calculate the fraction of ionized sites α

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along a polyelectrolyte chain. For this calculation, the second term on the righthand side of the equation must be multiplied by a factor of 2.

Since the propagation rate constant k_p is lower for propagation reactions involving the acrylate anion (Kabanov et al., 1973), increasing the fraction of ionized monomer by addition of base slows down the polymerization reaction. A similar pH dependence of the radical termination kinetics is expected. The conformation adopted by the propagating macroradical chain also depends on the pH of the reaction solution. As the pH is raised, intramolecular electrostatic interactions become more significant, and the chains adopt a more extended conformation. This effect leads to an increased polymerization rate as the radical propagation site becomes more accessible to surrounding monomer (Kabanov and Topchiev, 1971) and acts to mitigate repulsive effects between radical and anionic monomer.

Autoacceleration phenomena may also be important to the AA polymerization kinetics, due either to a temperature rise accompanying the highly exothermic reaction, or to the Trommsdorff or gel effect. In the case of the gel effect, diffusional limitations which arise over the course of polymerization lead to a decrease in k_t, the kinetic constant for the bimolecular radical termination reaction. The decrease in k_t causes a corresponding increase in the polymerization rate over time. Because of the gel effect, the kinetics of AA polymerizations depend on the concentration of cross-linking agent employed.

The kinetics of solution polymerizations involving AA have been studied previously by a number of investigators. The effects of varying the pH and other reaction parameters in homopolymerizations of AA at concentrations around 1 M and less have been examined (Ito et al., 1955; Kabanov et al., 1971, 1973, 1975). Ionization effects in AA copolymerizations with other difunctional monomers have also been determined (Cabaness et al., 1971; Ponratnam and Kapur, 1976, 1977). Finally, copolymerizations with a multifunctional cross-linking agent have been investigated at various extents of neutralization in order to model the dependence of structural properties in the gel product on the pH of the reaction solution (Zhao et al., 1995).

The prior work has shown that as the initial pH is varied in AA polymerization systems, the reaction rate passes through a minimum around pH 7 (Ito et al., 1955; Kabanov et al., 1971, 1973, 1975; Zhao et al., 1995). It was postulated that the pH dependence in the low pH regime is governed by monomer reactivity considerations and that added salt effects are important at elevated pH (Kabanov et al., 1973). It was also demonstrated that the dependence of the AA polymerization rate on the monomer concentration is greater than first order (Ito et al., 1955; Kabanov et al., 1971, 1973, 1975). Zhao et al. (1995) showed that monomer conversions substantially less than 100% are observed in AA cross-linking polymerizations and formulated a kinetic model describing the evolution of the network structure.

The AA polymerization kinetics, however, have not been studied at monomer concentrations above 1.2 M, and no attempt has been made to determine whether the pH dependence of the polymerization rate might vary as other reaction parameters are adjusted. Also, the conversion dependence of the AA polymerization rate (that is, the significance of the gel effect in AA reactions) has never been investigated.

The present work involved characterization of the kinetics of thermally initiated polymerizations of AA at industrially relevant monomer concentrations. The interdependent effects of solution pH, AA concentration, ammonium persulfate (APS) initiator concentration, and temperature were examined. Additionally, experiments were performed both in the presence and in the absence of a cross-linking agent. The polymerizations were studied using differential scanning calorimetry (DSC), which allowed for a determination of the conversion dependence of the reaction kinetics. It was important to quantify the effects of the various reaction parameters and the extent of reaction on the rate of polymerization because many of the structural properties of the gel product are determined by the polymerization rate.

Experimental Part

Acrylic acid (AA, Aldrich, Milwaukee, WI) was vacuum distilled at 27°C/2.5 mm Hg (0.33 kPa) prior to use in order to remove methoxyphenol inhibitor. Solutions were prepared by mixing AA, a quantity of concentrated NaOH (Mallinckrodt, Paris, KY) solution sufficient to give the desired extent of neutralization, and deionized water in a tared volumetric flask. For example, a 4.38 M AA solution with extent of neutralization $\alpha \cong 1$ was prepared by adding ~ 18 mL of 12 N NaOH solution to 15.0 mL of AA in a 50 mL volumetric flask. The mixture was then diluted to the line with deionized water. Addition of water to the AA in the flask prior to the addition of base allowed for better control of the exothermic neutralization reaction and prevented precipitation of sodium acrylate upon neutralization. The total solution weight was measured and an AA concentration (w/w) was calculated. Solutions with different α values were prepared in analogous fashion, using varying amounts of NaOH solution. Solutions having lower monomer concentrations were prepared by dilution of the 4.38 M solutions.

To carry out the reactions, ammonium persulfate (APS, Mallinckrodt) was added to a measured quantity of monomer solution in a polypropylene vial. In a typical example, 0.0106 g of APS was added to 4.0 mL of monomer solution, giving an initiator concentration of 1.16×10^{-2} M. The vial was sealed and shaken to dissolve the initiator, and nitrogen was bubbled through the solution to remove oxygen, which inhibits free radical polymerization. The pH of the deoxygenated solution was then measured using a pH meter (model SA 230, Orion Research, Cambridge, MA).

Cross-linking reactions were studied, varying the cross-linking ratio X over the range 0.00308–0.0626. For the cross-linking reactions, a quantity of trimethylolpropane triacrylate (TMPTA, Polysciences, Warrington, PA) sufficient to give the desired value of X was dissolved in AA and mixed with an aqueous solution of APS. The solutions were deoxygenated as above.

Reaction rate profiles were obtained using a differential scanning calorimeter (model DSC 910, TA Instruments, New Castle, DE). A hermetically sealed aluminum pan containing 5 to 10 mg of the monomer solution to be studied was placed in the DSC cell along with an empty reference pan. The cell was then heated at a rate of 5°C/min to the desired isothermal reaction temperature. Once the cell reached the reaction temperature, the DSC's nitrogen purge was turned on, and the reaction began. The temperature rise during the course of the reaction was less than 3°C for all reactions, and less than 1°C for all but the most highly concentrated reaction solutions.

The DSC was used to measure the heat flow from the sample pan relative to that from the reference pan over time. To analyze the data, a liner baseline corresponding to the heat flow at the end of the reaction was chosen. The heat flow due to reaction at any given time, that is, the difference between the measured heat flow at any given time and the baseline heat flow, was related to the rate of polymerization at that time using theoretical reaction enthalpies calculated from the known heats of polymerization of the monomers: -18.5 kcal/mol for AA (McCurdy and Laidler, 1964) and -20.6 kcal/mol for TMPTA (Moore, 1977). For example, a 20 wt. % AA solution would have a theoretical reaction enthalpy of 215 J/g. The total measured heat flow over the course of a polymerization carried out to 100% double bond conversion would be the product of the theoretical reaction enthalpy and the sample weight. As the measured rate of polymerization is equal to the first derivative of the double bond conversion p with respect to time, p was determined as a function of reaction time by integration of the R_p vs. time curves.

For the kinetic studies, polymerization solutions were prepared having different monomer concentrations, initiator concentrations, cross-linking ratios, and extents of neutralization. Additionally, reactions were carried out at several different temperatures. The effects of the various reaction conditions on the polymerization kinetics were studied by comparing the rate profiles obtained by DSC.

In order to establish the reproducibility of the experimental method and to provide an indication of the significance of experimental error when comparing rate profiles obtained under different reaction conditions, several experiments were performed for each set of conditions studied. The heat flux information from each experiment was used to prepare a plot of R_p as a function of p, and an average rate profile was calculated for each set of reaction conditions by averaging the R_p values from replicate experiments at 2% steps along the double bond conversion axis. The dependence of the polymerization rate on the various reaction parameters was analyzed by comparing average rate profiles. Additionally, average values of the initial and maximum polymerization rates were calculated for each set of reaction conditions. A pooled value of the standard deviation was calculated and used to determine 95% confidence limits for the rate data.

Results and Discussion

Rate dependence on solution pH

The dependence of the polymerization rate on the pH of the reaction solution was studied by performing DSC experiments over a range of pH values, at constant monomer concentration, initiator concentration, and reaction temperature. Figure 1 gives the average rate profiles for all pH values studied over the pH range 2.11–5.70. Clearly, below pH 6 the polymerization rate at constant monomer concentration (2.91 M) and initiator concentration (0.0116 M) is a decreasing function of the solution pH. This dependence is similar to that found previously for less highly concentrated systems (Zhao et al., 1995; Kabanov et al., 1973; Ito et al., 1955; Manickam et al., 1979) and can be explained in terms of the increasing importance of reactions and interactions between ionized species as the solution pH is raised. The overlap of the rate profiles for the pH 4.62 solution and the pH 5.28 solution is due to the fact that changes in rate behavior brought about by pH changes of less than one pH unit are on the order of the reproducibility limits of the experimental method (Scott, 1996).

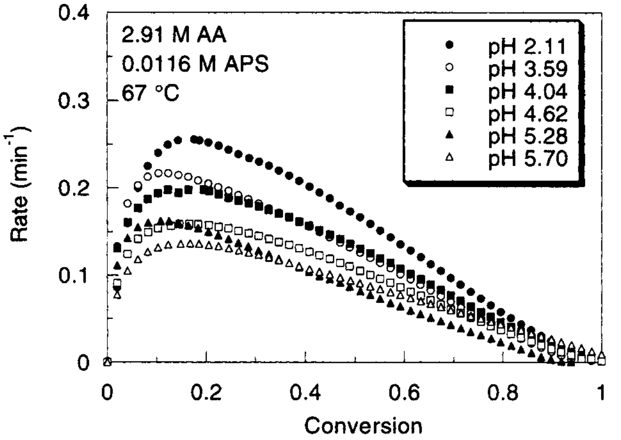

Figure 1. pH-dependent polymerization rate as a function of double bond conversion below pH 6.
Rate profiles shown are averages over several runs.

Additional experiments were performed in order to obtain kinetic data for polymerization solutions containing AA existing predominantly or exclusively in its ionized form. These experiments were carried out at solution pH values ranging from 6.44 to 11.94. The Henderson-Hasselbach equation predicts an extent of neutralization $\alpha > 0.99$ for an AA solution at pH 6.44. The average rate profiles obtained from the heat flow data are compared in Figure 2.

Comparison of the results presented in Figure 1 for solutions with $\alpha < 0.99$ and in Figure 2 for solutions with $\alpha > 0.99$

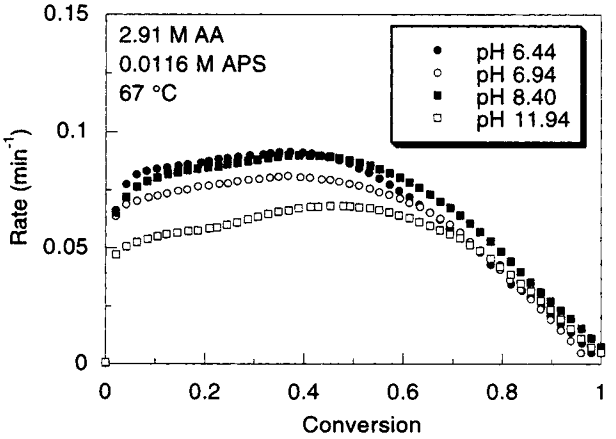

Figure 2. pH-dependent polymerization rate as a function of double bond conversion above pH 6.
Rate profiles shown are averages over several runs.

shows that above pH 6, the reaction rate depends less strongly on pH than at lower pH values. When the pH is raised ~ 3.5 pH units from 2.11 to 5.70, the maximum polymerization rate is reduced from 0.255 min^{-1} to 0.137 min^{-1}. However, when the pH is raised 5.5 pH units from 6.44 to 11.94, the maximum polymerization rate is reduced from 0.0914 min^{-1} to 0.0685 min^{-1}. Additionally, the maximum polymerization rate at pH 8.40 exceeds that observed at pH 6.94 and is nearly equal to that observed at pH 6.44.

In order to more quantitatively compare the pH dependence of the polymerization rate at a monomer concentration of 2.91 M to that determined previously for less highly concentrated systems (Zhao et al., 1995; Kabanov et al., 1973; Ito et al., 1955; Manickam et al., 1979), the initial rate of polymerization $R_{p,i}$ was calculated at several pH values over the studied pH range. In order to exclude initiation effects, $R_{p,i}$ was taken as the polymerization rate at 5% monomer conversion (observed at polymerization times of 0.70–1.3 min), and Table 1 gives $R_{p,i}$ for each pH value. The table also gives the ratio $k_p/k_t^{1/2}$, the maximum value of the polymerization rate at each pH, $R_{p,\max}$, and the double bond conversion at which $R_{p,\max}$ was observed. The ratio $k_p/k_t^{1/2}$ was calculated from the initial rate data. For this calculation, it was necessary to account for the pH dependence of the initiator dissociation constant k_d (Kolthoff and Miller, 1951; Behrman and Edwards, 1980). A value of $7.2 \times 10^{-5}\ \text{s}^{-1}$ was used for the pH 2.11 solution, where the acid-catalyzed APS decomposition pathway was assumed to be important (Behrman and Edwards, 1980). For all other pH values, a value of $1.4 \times 10^{-5}\ \text{s}^{-1}$ was used for k_d. The k_d values were calculated from tabulated k_d and activation energy data (Kolthoff and Miller, 1951). The k_d value used above pH 3 was that for solutions with pH 13. The use of a single value for k_d above pH 3 is an approximation that leads to a positive bias in calculated $k_p/k_t^{1/2}$ values, since k_d varies slightly with pH even in neutral and weakly basic solutions.

Table 1 also gives values of the number average molecular weight $\overline{M}_n$. These data were calculated from the kinetic chain length, derived from the rate and rate constant data (Odian, 1991). Termination by recombination was assumed.

Figure 3 gives the ratio of $R_{p,i}$ to the minimum value of $R_{p,i}$ (pH 11.94) as a function of solution pH. This presentation allows for ready comparison of the results from this study to the data of Kabanov et al. (1973) and the data of Zhao et al. (1995). The experiments of Kabanov et al. were carried out with an initial monomer concentration, $[M]_0$, of 1.2 M and an AIBN initiator concentration of 0.005 M; the experiments of Zhao et al. were carried out with $[M]_0 = 0.63$ M and a KPS initiator concentration of 0.00094 M.

Table 1. Average Value of $R_{p,i}$ as a Function of Solution pH*

pH	$R_{p,i}$ (min^{-1})	$R_{p,\max}$ (min^{-1})	Conv. at $R_{p,\max}$	$k_p/k_t^{1/2}$ $(\text{L/mol·s})^{1/2}$	$\overline{M}_n \times 10^{-3}$ (g/mol)
2.11	0.183	0.255	0.169	3.52	765
	(±0.018)	(±0.018)		(±0.34)	(±130)
5.70	0.112	0.137	0.147	4.89	2,420
	(±0.015)	(±0.015)		(±0.65)	(±560)
6.94	0.0699	0.0810	0.349	3.07	1,500
	(±0.0182)	(±0.0182)		(±0.79)	(±670)
8.40	0.0737	0.0959	0.396	3.21	1,590
	(±0.0115)	(±0.0115)		(±0.48)	(±410)
11.94	0.0517	0.0685	0.430	2.25	1,110
	(±0.0182)	(±0.0182)		(±0.78)	(±670)

*Various other kinetic parameters, as described in the text, are also given. Values in parentheses are 95% confidence limits ([AA] = 2.91 M, [APS] = 0.0116 M, 67°C).

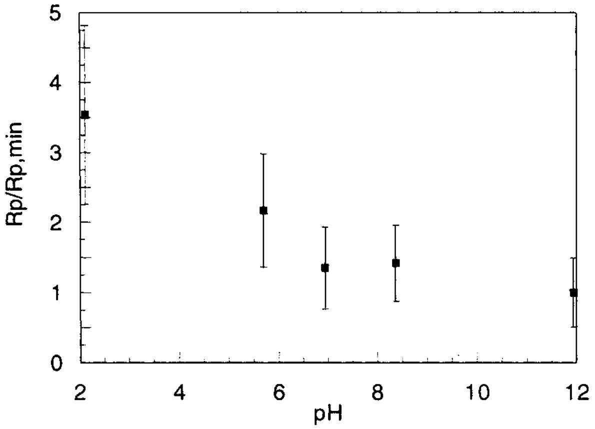

Figure 3. AA initial polymerization rate normalized by the minimum initial rate as a function of solution pH for solutions with monomer concentration 2.91 M.

Error bars represent 95% confidence limits.

In comparing the pH dependence described in Figure 3 for 2.91 M AA solutions to that for less concentrated systems, a number of important differences in kinetic behavior become apparent. First of all, the previous results indicate a 25- to 70-fold decrease in the polymerization rate upon raising the solution pH from ~ 2.0 to ~ 7.0. As shown in Figure 3, the rate changes by a factor of at most 3 when the solution pH is raised from ~ 2.0 to ~ 7.0 in the present study. Thus, the polymerization rate depends less strongly on the pH of the reaction solution when the initial monomer concentration is 2.91 M than when the AA concentration is on the order of 1 M or less. One can conclude that the kinetic constants depend not only on the pH of the reaction solution, but also on the monomer concentration. As the monomer concentration is increased, the concentration dependence of the kinetic constants dominates the pH dependence.

Indeed, the data of Table 2 offer further support for the notion of concentration-dependent kinetic constants. The table provides initial rate data for solutions with pH values nearly equal to 2 and nearly equal to 5, at various monomer and initiator concentrations. Solution 1 in Table 2 is the solution whose rate behavior is described by Figure 3. The table clearly shows that the polymerization rate is affected more dramatically by a change in pH from ~ 2 to ~ 5 at lower monomer and initiator concentrations.

Figure 3 also shows that when the initial AA concentration is 2.91 M, $R_{p,i}$ decreases almost continuously to a minimum around pH 12. The decrease in rate with increasing pH is clearly less dramatic at higher pH values. This behavior is markedly different than that reported previously for systems with monomer concentrations around 1 M. Since the pH dependence at elevated pH is governed by counterion shielding effects (Kabanov and Topchiev, 1971; Zhao et al., 1995), the results suggest that the effects of added cation are less important at higher monomer concentrations. This can be attributed to the fact that the propagating radical is less acces-

Table 2. $R_{p,i}$ **at Various Values of [AA] and [APS] (mol/L)***

Solution	[AA]	[APS]	$R_{p,i}$ (min^{-1}) (pH)	$R'_{p,i}$ (min^{-1}) (pH)	$R_{p,i}/R'_{p,i}$
1	2.91	0.0116	0.183±0.018 (2.11)	0.112±0.015 (5.70)	1.63±0.27
2	1.45	0.0119	0.197±0.018 (2.17)	0.0822±0.0148 (5.04)	2.40±0.20
3	1.45	0.00580	0.132±0.018 (2.21)	0.0323±0.0182 (5.24)	4.09±2.37
4	4.38	0.0118	0.190±0.018 (2.05)	0.131±0.015 (5.56)	1.45±0.21
5	4.38	0.0175	0.190±0.015 (2.00)	0.172±0.011 (5.57)	1.11±0.11

*Rate data are given for two pH values at each concentration point, and the right-most column gives the ratio of $R_{p,i}$ at the lower pH to $R_{p,i}$ at the higher pH. Rate data represent average values, and 95% confidence limits are given. Data taken at 67°C.

sible to the monomer at higher concentrations. Although the macroradicals adopt a more extended conformation with increasing ionization, access to the propagation site is limited by the high local concentration of neighboring radical chains. In essence, at higher monomer concentrations, the local environment of propagating radicals does not change significantly upon uncoiling of the radical chains. Therefore, the radical reactivity is not greatly affected by the shielding effects associated with addition of cationic species to the system.

Autoacceleration of the polymerization rate

Careful examination of the data presented in Table 1 reveals that the value of $R_{p,\max}$ for each polymerization is larger than the initial polymerization rate $R_{p,i}$. Therefore, autoacceleration is occurring, that is, the polymerization rate actually increases with increasing monomer conversion over a portion of the conversion profile. In the case of bulk polymerizations, this phenomenon is typically attributed to the gel effect (Anseth et al., 1994a,b, 1995; Kurdikar and Peppas, 1994; Scranton et al., 1992). The polymerization rate increases over time due to a decrease in the termination rate constant as the reaction medium becomes increasingly viscous. The polymerization rate begins to decrease only when the monomer is sufficiently depleted and/or when the propagation reaction becomes diffusion-limited due to diffusional limitations on the monomer (Scranton et al., 1992).

In this context, the observed shift in the conversion corresponding to $R_{p,\max}$ between pH 5.70 and pH 6.94, seen in Table 1, warrants some attention. The monomer conversion at which the polymerization rate begins to decrease more than doubles as the pH passes through the region corresponding to 100% ionization of the polymer. This shift in the location of $R_{p,\max}$ suggests that the observed autoacceleration of the polymerization rate occurs for different reasons in the two pH regimes.

In fact, comparison of the rate profiles in the low pH regime to those in the high pH regime shows that the reaction exotherms have distinctly different shapes in each pH regime. Below pH 6, the reaction rate increases sharply over the initial conversion region, in each case reaching a maximum at around 15% conversion. The reaction rate then decreases over the duration of the polymerization. When the pH is higher than pH 6, the polymerization rate again initially undergoes a sharp (and more short-lived) increase. However, this initial sharp increase is followed by a second, more gradual increase in the polymerization rate. The rate reaches a maximum at conversions around 40%. The AA polymerization behavior observed in the high pH regime is similar to that observed in the bulk homopolymerization of multifunctional acrylates and methacrylates (Anseth et al., 1994a,b, 1995; Kurdikar and Peppas, 1994; Scranton et al., 1992). Diffusional considerations are known to play a strong role in these latter systems.

The differences in the kinetic features of the polymerization in the two pH regimes can be explained in terms of a mechanistic picture which incorporates two different modes of autoacceleration. The initial sharp rise in polymerization rate, observed at all pH values, is due to localized nonisothermality. Early on in the polymerization, when heat is evolved most quickly, the measured temperature increases by an amount on the order of 0.5°C. It is not unreasonable to expect that local temperature variations will be even greater. The kinetic constants therefore will increase slightly over time, giving a maximum at low conversion. For this reason, it is quite expected that the length of time over which the reaction rate increases sharply is highest at low pH, when the initial rate of heat evolution is greatest. It is also possible that loss of solvent due to evaporation contributes to rate acceleration in the early stages of polymerization.

In the case of solutions with pH greater than 6, however, diffusional effects complicate the picture. The data of Kabanov et al. (1973) show that the specific viscosity of AA polymerization solutions increases above pH 6, as polymer chains uncoil. Due then to a coupling of the effects of a rapidly evolving reaction medium and the effects of electrostatic interactions between charged macroradicals, radical diffusion becomes increasingly hindered as the reaction proceeds. As a result, the polymerization rate in the high pH regime is marked by a gradual increase with increasing conversion, after the initial sharp rise in the polymerization rate. The gel effect at high pH is clearly evident in Figure 4, which gives monomer conversion as a function of time for various values of pH. The slopes of the curves for solutions with pH 6.94 and higher gradually increase with conversion before de-

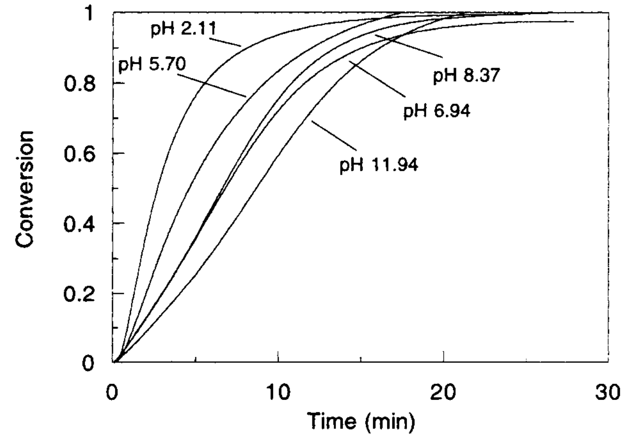

Figure 4. Time-dependent fractional double bond conversion for solutions at several pH values, all with initial AA concentration 2.91 M.

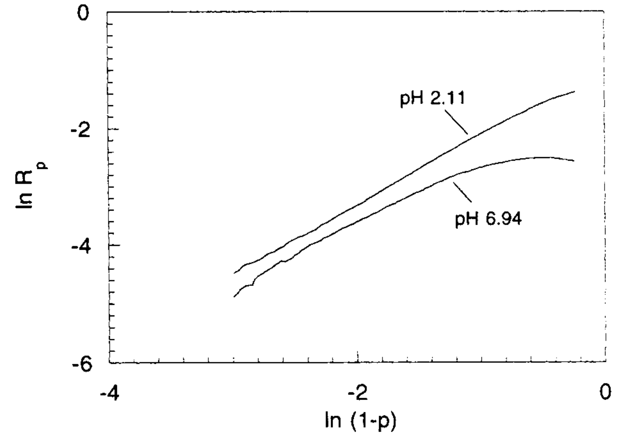

Figure 5. Conversion dependence of the polymerization rate in the polymerization of 2.91 M AA solutions.

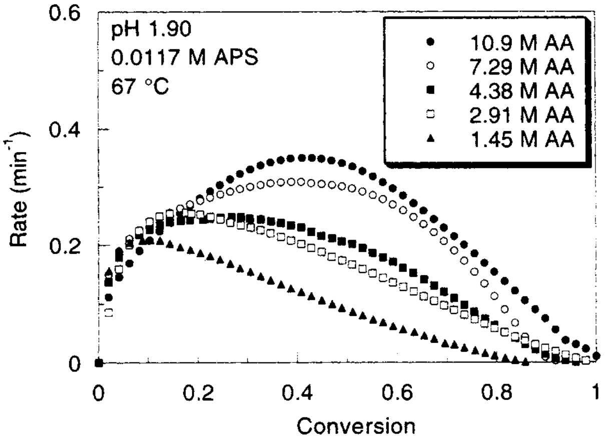

Figure 6. $[M]_0$-dependent polymerization rate as a function of double bond conversion (unneutralized AA solutions).

Rate profiles shown are averages over several runs.

creasing due to depletion of monomer. No such increase is seen in the curves for lower pH values.

In Figure 5, ln R_p is plotted as a function of ln (1-p) over the conversion range 0.20–0.95 for 2.91 M AA solutions at pH 2.11 and at pH 6.94. The lower conversion limit was chosen to avoid the region of rate increase due to nonisothermality. As shown in the figure, ln R_p depends linearly on ln (1-p) at pH 2.11. Linear regression on the data at pH 2.11 gives a correlation coefficient of 0.998. The linear dependence indicates that the kinetic constants do not depend on conversion. At pH 6.94, the dependence of ln R_p on ln (1-p) is clearly nonlinear, indicating that the kinetic constants do depend on conversion when the pH of the polymerization solution is sufficiently high that ionized macroradicals exist in an extended conformation. However, the pH 6.94 curve does become linear in the latter stages of the polymerization. This result suggests that the viscosity of the polymerization solution increases to a limiting value at a double bond conversion substantially less than 100%. Beyond this conversion, the termination kinetics are unaffected by additional reaction.

Rate dependence on initial monomer concentration

As radical mobility, and hence the nature and extent of the gel effect, vary with solution concentration, the kinetic features of the polymerization depend strongly on $[M]_0$. The initial rate of heat release, and thus the significance of nonisothermal reaction behavior, also depend on $[M]_0$. The dependence of the polymerization kinetics on $[M]_0$ was studied by performing DSC experiments over a range of initial AA concentration values, at constant initiator concentration and reaction temperature. Concentration effects were examined both for unneutralized (pH ~ 2.0) and for mostly neutralized (pH ~ 5.5) AA solutions. The average rate profiles for solutions with various initial monomer concentrations are compared in Figures 6 and 7, which clearly show that the value of the initial monomer concentration profoundly affects the kinetics of the polymerization. In both plots, those polymerizations carried out at higher monomer concentrations achieve higher values of $R_{p,\max}$. Additionally, the conversion corresponding to $R_{p,\max}$ increases as the monomer concentration increases.

As the value of $R_{p,\max}$ is a measure both of the initial polymerization rate and of the extent to which autoacceleration is occurring in the polymerization system, it is important to examine the dependence of $R_{p,\max}$ on $[M]_0$ in some detail. Figure 8 provides plots of $R_{p,\max}$ as a function of $[M]_0$ for the rate profiles given in Figures 6 and 7. $R_{p,\max}$ increases nearly linearly with monomer concentration in both neutralization regimes. The dependence of $R_{p,\max}$ on $[M]_0$ is a result not predicted by the classical rate expression for free radical polymerization. The unusual dependence arises because the decomposition of persulfates is accelerated in the presence of acrylic acid (Zhao et al., 1995). The increase in the maximum rate is due to an increase in the rate of initiation when the initial monomer concentration is raised. In this sense, the increase in $R_{p,\max}$ with increasing $[M]_0$ is analogous to the increase in $R_{p,\max}$ observed during the homopolymerization of monomethacrylates upon raising the initiator concentration (Scranton et al., 1992). The concentration dependence of

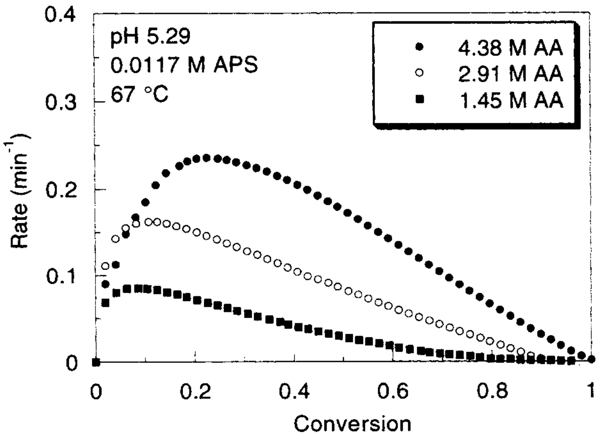

Figure 7. $[M]_0$-dependent polymerization rate as a function of double bond conversion (mostly neutralized AA solutions).

Rate profiles shown are averages over several runs.

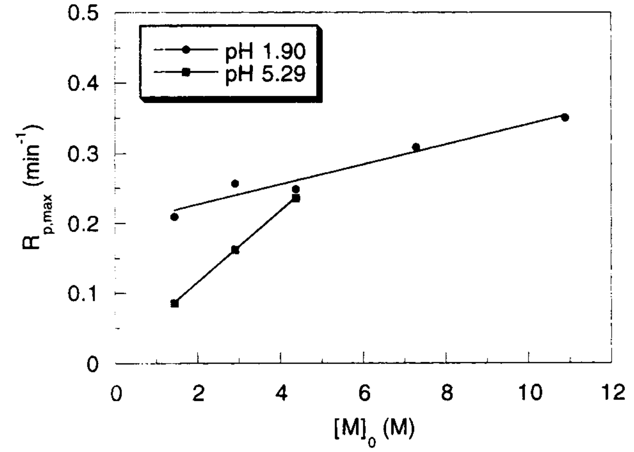

Figure 8. Maximum polymerization rate $R_{p,max}$ as a function of initial monomer concentration.

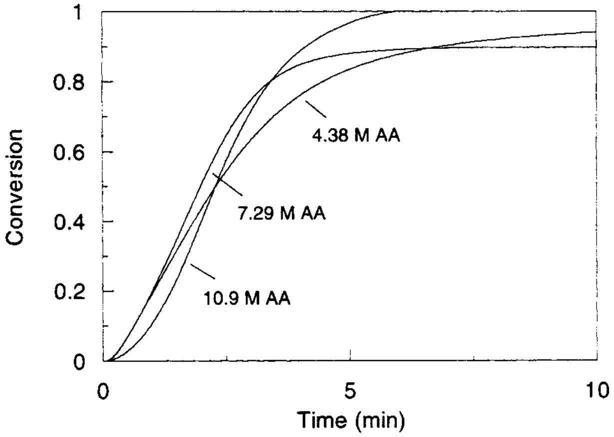

Figure 9. Time-dependent fractional double bond conversion for unneutralized AA solutions at various values of $[M]_0$.

$R_{p,max}$ also arises due to the greater importance of diffusional considerations as $[M]_0$ is increased.

Because of the dependence of the initiation rate on the monomer concentration and because of the greater impact of the gel effect at higher monomer concentrations, the dependence of the overall polymerization rate on $[M]$ is greater than first order. Indeed, the slope of the linear curve in Figure 5 is 1.1578; the slope of the linear region of the other curve is 1.2468. The slope is a measure of the order of the reaction with respect to $[M]$.

Also, Figure 8 shows that the difference in maximum polymerization rates between pH ~ 2.0 and pH ~ 5.0 decreases as the initial monomer concentration is increased. At $[M]_0 =$ 4.38 M (~ 30 wt. %), the maximum rates are nearly identical at the two pH values (see also Table 2). These results again suggest that at higher monomer concentrations, the concentration dependence of the kinetic constants dominates the pH dependence. More specifically, one expects k_t to depend much more strongly than k_p on the initial monomer concentration due to diffusional effects on the termination kinetics. Because of electrostatic interactions between propagating radicals, k_t will also depend on the solution pH. Then, as $[M]_0$ is increased, k_t decreases more for solutions at high pH than for solutions at low pH. The result is that the pH dependence of the polymerization rate (dictated at lower values of $[M]_0$ by the variation of k_p with α) is diminished at higher values of $[M]_0$.

The shift of the location of $R_{p,max}$ to higher conversions as the monomer concentration is increased, as seen in Figures 6 and 7, is another indication that the termination kinetics depend on $[M]_0$. In fact, careful examination of Figure 6 reveals that unneutralized AA solutions at $[M]_0 = 7.29$ M [~ 50 wt. %] and $[M]_0 = 10.9$ M [~ 75 wt. %] exhibit polymerization behavior suggestive of a significant gel effect. The polymerization rate undergoes a rapid increase initially, followed by a more gradual increase to a maximum around 40% monomer conversion. This behavior is similar to that exhibited by 2.91 M solutions above pH 6, where the viscosity of the reaction medium and the accompanying effects on the termination kinetics cause the polymerization rate to increase with conversion. Clearly, raising $[M]_0$ to around 7.29 M and higher results in diffusion-controlled termination kinetics, as well. Figure 9 provides plots of conversion as a function of time for the unneutralized AA solutions with initial monomer concentrations of 4.38 M, 7.29 M, and 10.9 M. The curves at $[M]_0 = 7.29$ M and $[M]_0 = 10.9$ M show the gradual increase in slope with increasing conversion characteristic of the gel effect. The reasons that limiting conversions are reached in some cases and that the value of the limiting conversion varies are not clear

Table 3 summarizes the various conditions of pH and monomer concentration under which the gel effect is observed in AA polymerizations. Recall that the pH dependence of the gel effect arises due to the increase in solution viscosity accompanying chain uncoiling above pH 6. The concentration dependence arises due to the obvious relationship between viscosity and solution concentration.

Rate dependence on APS initiator concentration

Since the rate of free radical polymerization is proportional to $R_i^{1/2}$, where R_i is the rate of initiation, increasing the initial APS initiator concentration [APS] increases the rate of AA solution polymerization (Figure 10). Average rate profiles are provided in the figure for unneutralized AA solutions at three different APS concentrations: 0.0116 M, 0.00603 M, and 0.00230 M. The corresponding weight concentrations are 1.3%, 0.7%, and 0.3%, based on monomer weight.

The polymerization rate obviously increases with increasing [APS]. Figure 10 shows that as the initiator concentration is lowered below 0.0116 M, limiting monomer conversions less than 100% are observed. Because the decomposition of APS is accelerated in the presence of acrylic acid, all of the initiator is consumed prior to completion of the polymerization (Odian, 1991; Zhao et al., 1995). This phenomenon is known as dead-end polymerization and depends for obvious reasons

Table 3. Conditions of pH and Monomer Concentration Under which the Gel Effect is Observed in AA Polymerizations

	pH < 6	pH > 6
[M] < 50 wt. %	No gel effect	Gel effect
[M] > 50 wt. %	Gel effect	Gel effect

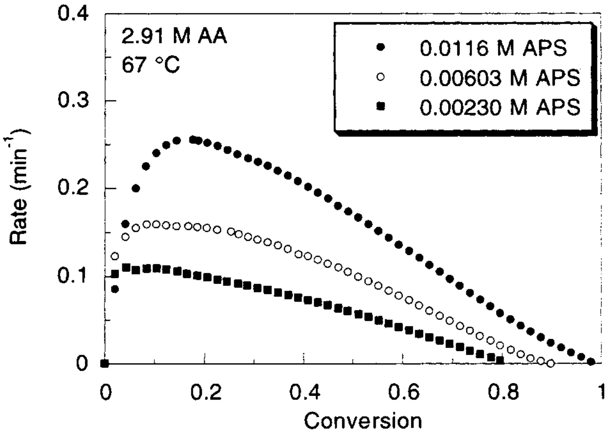

Figure 10. [APS]-dependent polymerization rate as a function of double bond conversion for unneutralized solutions.

Rate profiles shown are averages over several runs.

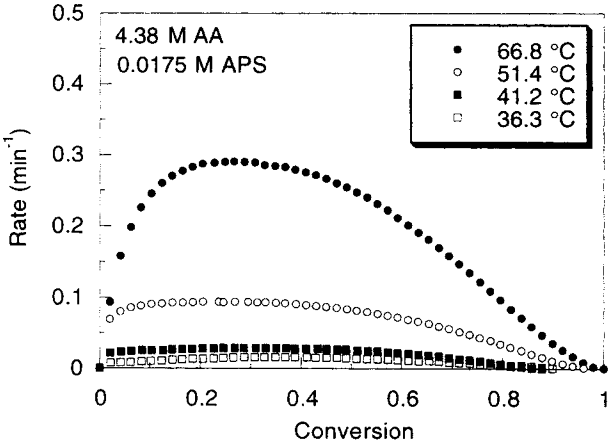

Figure 11. Temperature-dependent polymerization rate as a function of double bond conversion for unneutralized solutions.

Rate profiles shown are averages over several runs.

on the initiator concentration. The fact that the polymerization rate depends on $[APS]^{1/2}$ was demonstrated by plotting ln $R_{p,i}$ as a function of ln [APS]. The slope of the line drawn through the data points was 0.506; the correlation coefficient was 1.00. The slope of the line is a measure of the order of the polymerization rate with respect to [APS].

Rate dependence on polymerization temperature

The dependence of the kinetics of free radical polymerizations on the temperature of polymerization is described by the Arrhenius relationship for the kinetic constants k_p, k_t, and k_d. The dependence of the AA polymerization kinetics on the reaction temperature was studied by performing DSC experiments at several different temperatures, while keeping the initial monomer concentration, the initiator concentration, and the extent of neutralization constant. Temperature effects were examined using unneutralized 4.38 M AA solutions, with an APS concentration of 0.0175 M. The average rate profiles for the experiments performed at various temperatures are compared in Figure 11.

Figure 11 shows that the polymerization rate depends strongly on the polymerization temperature. Indeed, $R_{p,i}$ increases nearly 20-fold, from 0.00464 min^{-1} to 0.0827 min^{-1}, when the polymerization temperature is raised from 36.3°C to 51.4°C. $R_{p,i}$ increases over 2-fold, to 0.190 min^{-1}, when the polymerization temperature is raised from 51.4°C to 66.8°C. Figure 12 shows the dependence of ln $R_{p,i}$ on (1/RT); a linear regression calculation on the data gives $r^2 = 0.885$. For an Arrhenius-type dependence of the kinetic constants on temperature, a linear dependence is expected, and the overall activation energy E_R is given by the slope. E_R contains contributions from the activation energies for propagation, termination, and initiator dissociation. The measured slope gives a value for E_R of 98.1 kJ/mol, outside the range expected for thermally initiated free radical polymerizations (Odian, 1991). This result is not surprising, given the extent to which the curve deviates from linearity.

A linear regression calculation using all of the data in Figure 12 except that taken at 36.3°C gives $r^2 = 0.961$. The temperature dependence of the kinetic constants is most accurately described by the Arrhenius model at higher temperatures. This result suggests that when the temperature is sufficiently low, E_R becomes temperature dependent, causing a change in the observed slope of the Arrhenius plot. The observed variation in E_R at lower temperatures is most likely due to the increased solution viscosity at these temperatures. Indeed, Figure 11 shows that at 36.3°C and 41.2°C, limiting monomer conversions less than 100% are observed. The existence of limiting conversions suggests that at low temperatures and high conversions, when the reaction medium is most viscous, the propagation reaction becomes diffusion-limited due to diffusional limitations on the monomer.

Rate dependence on TMPTA cross-linking agent concentration

The dependence of the strength of the gel effect on the cross-linking ratio X (mol/mol) was studied in experiments using cross-linking agent TMPTA. Figure 13 shows conver-

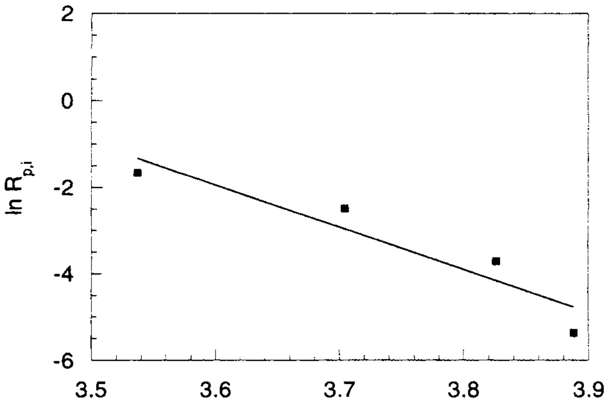

Figure 12. Temperature dependence of $R_{p,i}$.

Data points are for experiments performed at 36.3°C, 41.2°C, 51.4°C, and 66.8°C.

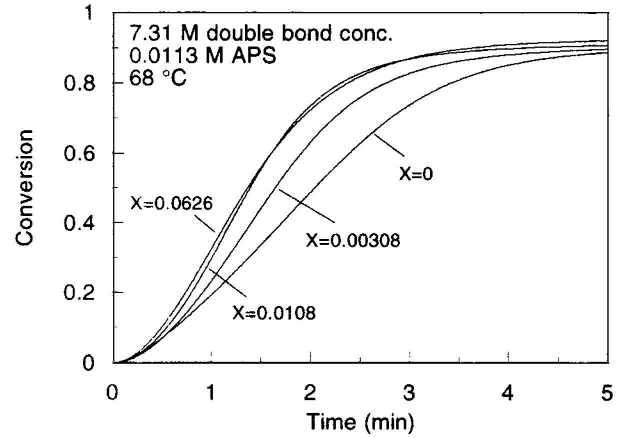

Figure 13. Time-dependent fractional double bond conversion for unneutralized solutions at various values of *X* (cross-linker TMPTA).

sion profiles for several X values at constant total double bond concentration (7.31 M). The increase in curve slope with time is more substantial at higher values of X, indicating a larger autoacceleration. However, the figure shows that although R_p initially increases more rapidly when $X = 0.0626$ than when $X = 0.0108$, the rate begins to decrease earlier on for the more highly cross-linked system and a smaller value of $R_{p,\max}$ is observed. This result can be attributed to the low solubility of TMPTA in aqueous reaction systems. At high concentrations of added TMPTA, the cross-linking ratio achieved during the polymerization will be significantly less than the nominal value calculated from the amount of TMPTA added (Bell, 1996).

Table 4 gives $R_{p,i}$ and the average time required to reach 1% double bond conversion (the induction time) for each value of X. The data show that the gel effect is important in AA cross-linking polymerizations from the beginning of the polymerization. In the absence of a gel effect, one would expect the values of $R_{p,i}$ and the induction time to remain constant with changing X, since the initial double bond concentration is held constant. However, $R_{p,i}$ increases significantly as X is raised, and the induction time decreases accordingly. These results indicate that the onset of the gel effect is almost instantaneous.

Conclusion

The kinetics of acrylic acid solution polymerizations depend strongly on the degree of ionization of AA in solution (that is, the solution pH), the initial AA concentration, the APS initiator concentration, the polymerization temperature, and the concentration of the multifunctional cross-linking agent TMPTA. The complex kinetic behavior can be fully understood only when the roles played by electrostatic interactions, chain conformation effects, and diffusional effects are considered.

The AA polymerization rate at elevated monomer concentrations decreases with increasing pH over all pH values. The dependence of the rate on pH is significantly weaker at elevated pH. Significantly, the dependence of k_p and k_t on solution pH is coupled to a substantial dependence on the initial AA concentration. When the monomer concentration is sufficiently high, the concentration dependence of the kinetic constants dominates the pH dependence. The kinetic constants also depend on monomer conversion with a gel effect observed when the initial monomer concentration is increased above 30 wt. % or at lower monomer concentrations when the pH is raised above pH 6. Because of the gel effect, the overall activation energy for polymerization varies slightly as the polymerization temperature is increased, due to the increased mobility afforded propagating radicals as the solution viscosity decreases. The impact of diffusional effects on the AA polymerization rate is increased upon addition of TMPTA. In AA cross-linking polymerizations, diffusional considerations are important from the outset of polymerization.

All of the experimental data, taken together, show that the AA polymerization system is most complex, with kinetic constants dependent not only upon temperature, but also upon solution pH, chain conformation, monomer concentration, cross-linking agent concentration, and double bond conversion.

Table 4. $R_{p,i}$ and Induction Time at Various Values of X*

X (mol/mol)	$R_{p,i}$ (min^{-1})	Induction Time (min)
0	0.162±0.018	0.27
0.00308	0.214±0.018	0.26
0.0108	0.258±0.018	0.17
0.0626	0.264±0.018	0.16

*Cross-linker was TMPTA, and the total double bond concentration for all polymerizations was 7.31 M ([APS] = 0.0113 M). Rate data represent average values, and 95% confidence limits are given. Data taken at 68°C.

Acknowledgment

This work was supported by grant No. CTS 93-11563 from the National Science Foundation.

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Manuscript received Feb. 26, 1996, and revision received July 5, 1996.