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Effects of Ionization on the Reaction Behavior and Kinetics of Acrylic Acid Polymerizations

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ABSTRACT: The kinetics of acrylic acid (AA) solution polymerization was investigated by polymerizing 30 wt % aqueous AA solutions at pH values ranging from 2.2 to 9.9. The polymerization rate was determined with differential photocalorimetry and was found to be a strong function of the solution pH and the ionic strength. Although the polymerization rate decreased with increasing pH below pH 6.5, an increase in the polymerization rate was observed as the pH was raised further, due to reduction in electrostatic repulsion. The propagation and termination constants were measured using an after-effect technique and were shown to depend strongly on monomer conversion, solution pH, and ionic strength.

Introduction

Polyacrylate materials are widely used as superabsorbents for the rapid absorption of large amounts of water and other biological fluids.[1,2] In addition, they have been used as important bioadhesive polymers,[3] as membranes for bioseparations,[4] and as carriers for controlled release devices.[5] They are usually produced by the reaction of partially neutralized acrylic acid (AA) using a variety of methods, as described by Buchholz.[6] Although a large number of patents has been issued concerning various industrial methods of poly(acrylic acid) (PAA) production,[7] little is known about the kinetics of such reactions.

Free radical polymerization reactions of AA have been investigated by a number of researchers. The earliest kinetic study is by Ito *et al.*,[8] who investigated the effect of pH on polymerization rate and showed that the latter decreased sharply from pH 2 to 6, and then increased from pH 6 to 10. Later, Kabanov *et al.*[9,10] studied the effective reactivity of the propagating radicals and established a slightly different dependence of the polymerization rate on pH. More recent studies of the effect of polymer concentration and salt concentration have been reported.[11,12]

In this work, we present a detailed analysis of the kinetics and kinetic constants in the photopolymerization of AA.

Experimental Section

Materials. Acrylic acid (AA, Aldrich, Milwaukee, WI) was purified by vacuum distillation. All other chemicals were used as received. Solutions were prepared by dissolving the monomer in deionized water to produce 4.4 M aqueous AA solutions (approximately 30 wt %). The pH of the solutions was controlled by the addition of NaOH (Aldrich, Milwaukee, WI). For example, a solution with degree of neutralization, α, approximately equal to 0.3 was prepared by the addition of NaOH until the molar ratio of the NaOH/AA in the final solution was equal to 0.3. The pH of the solutions was measured using a standard pH probe (Model SA 230, Orion Research, Cambridge, MA), and the exact value of α was calculated from the measured pH using the Henderson−Hasselbach equation.[13] In addition, the ionic strength of the solutions was varied by the addition of NaCl (Aldrich, Milwaukee, WI). The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorne, NY) was dissolved in the solutions at a concentration of 1 g of initiator/100 g of AA and used to initiate the polymerizations upon exposure to ultraviolet light.

Methods. Polymerization rate profiles were monitored with a differential photocalorimeter (DPC 930, TA Instruments, New Castle, DE). The light source was a 100 W mercury arc lamp, and neutral density filters (Melles Griot, Irvine, CA) were used to control the light intensity. Unless otherwise stated, all polymerizations were conducted at ambient temperature and initiated with approximately 16 mW/cm^2 of ultraviolet light.

Typically 4−6 mg of monomer solution was placed in an aluminum DPC pan and directly covered with a thin film of polypropylene. The purpose of this film was to eliminate any evaporation of the AA solution while the sample cell was flushed with nitrogen for 10 min prior to polymerization. The polymerizations were conducted in a nitrogen atmosphere since oxygen is a well-known inhibitor of free radical polymerizations.[14]

The heat flux measured by the DPC was proportional to the polymerization rate (related by the theoretical heat evolved per reacted double bond), and the total double bond conversion was determined by integrating the rate curve as a function of polymerization time. For the acrylic acid double bond, the theoretical heat evolved[15] per mole of reacted monomer was 18.5 kcal/mol. Finally, to determine the individual kinetic constants for propagation and termination, after-effect experiments were conducted in which the polymerization rates were monitored after ceasing exposure to the UV light and, therefore, stopping initiation at several different double bond conversions.

Results and Discussion

Kinetics Analysis. The polymerization behavior of AA is rather complex with many distinct and notable features, as illustrated in Figures 1 and 2. In general, the complexities that occur during the polymerization are the result of several factors, including partial or total dissociation of the acid functionality, leading to electrostatic interactions between reacting species, and the influence of ionic strength.[9]

The rate of polymerization was a strong function of solution pH for the polymerization of 30 wt % acrylic acid in water, as shown in Figure 1. The maximum polymerization rate decreased monotonically with increasing pH, as the fractional ionization of monomer increased. The observed pH effect is due to electrostatic repulsions between dissociated monomer molecules and charged sites along the backbone of the propagating radical chain. In addition, the inherent reactivity of the ionized AA monomer may be lower than that of the un-

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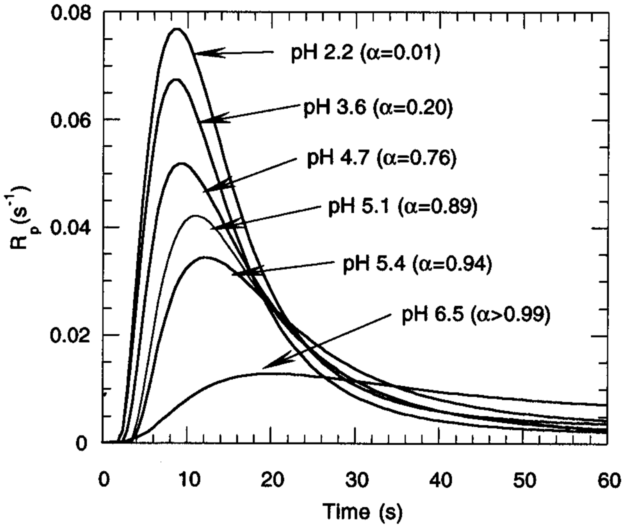


Figure 1. Polymerization rate, R_p, as a function of time for 30 wt % acrylic acid in water at varying pH values from 2.2 to 6.5. The calculated fractional monomer ionization, α, is given in parentheses after the measured pH.

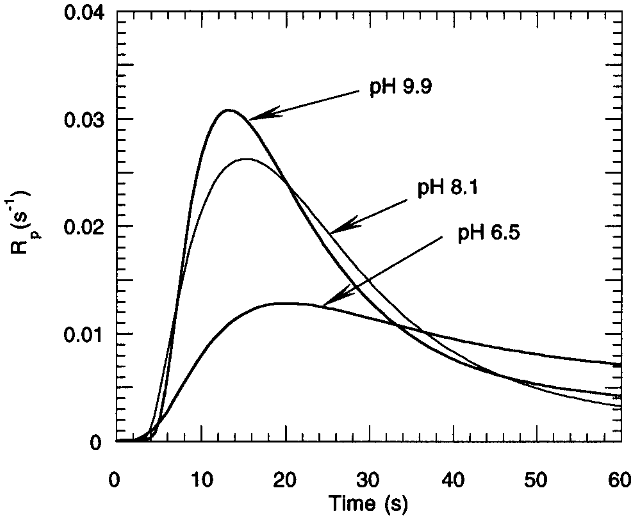


Figure 2. AA polymerization rate, R_p, as a function of time for 30 wt % acrylic acid in water at varying pH values from 6.5 to 9.9.

ionized monomer and may contribute to a lowering of the overall polymerization rate. As the solution pH approached 6.5, the polymerization rate dropped dramatically. Because most of the AA monomer molecules as well as a significant fraction of the pendant acid groups along the macroradical chain were ionized at that level (degree of neutralization, α, for monomer >0.99 at pH 6.5), it became exceedingly difficult for the propagation reaction to occur and the polymerization rate decreased. The termination kinetic constant also decreased (leading to increasing polymerization rate), but the dependence of the rate of polymerization on k_t was only to the half power so an overall decrease in the rate occurred.

However, as shown in Figure 2, when the pH was increased beyond pH 6.5, the polymerization rate did not continue to decrease, but rather, began to increase. This increase has been explained by others[9] as an ion-pairing effect that reduces the electrostatic repulsion between propagating species. At higher pH values, the increased cation concentration (due to added NaOH) causes a shielding effect or leads to ion pairs that enhance the polymerization rate. Thus, the behavior observed in Figures 1 and 2 is a combination of two effects: an increase in the number of charged molecules at higher values of pH that led to a decrease in the polymerization rate and an increase in the shielding of dissociated acid groups at higher ionic strengths (above pH 6.5) which enhanced the polymerization rate.

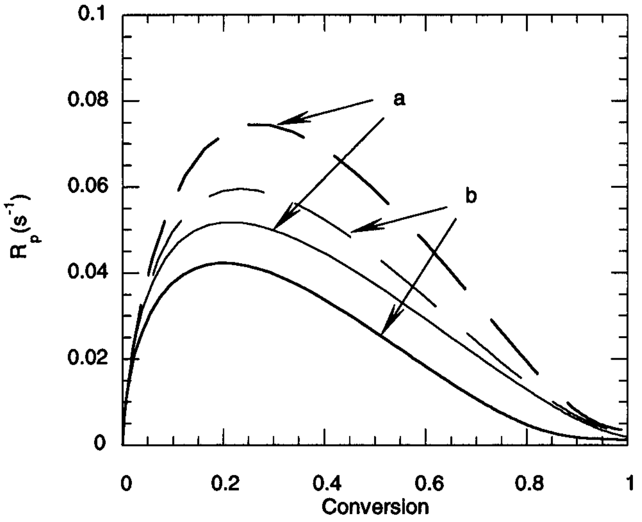


Figure 3. Polymerization rate for 30 wt % acrylic acid at pH 4.7 (a) and at pH 5.1 (b) as a function of conversion. Solid lines represent AA solutions neutralized with NaOH under conditions of variable ionic strength. Dashed lines represent AA solutions neutralized with NaOH under conditions of constant ionic strength achieved by addition of NaCl.

To isolate the effect of ionization on the reaction behavior, the polymerization profiles were also measured at constant ionic strength. Conditions of constant ionic strength were achieved by adding NaCl to the system so that the total concentration of NaCl and NaOH (used to vary the pH) was kept constant. The results are shown in Figure 3. At higher ionic strengths, solutions with pH 4.7 and pH 5.1 exhibited a large increase in the rate of polymerization. In fact, adding salt to the pH 4.7 system enhanced the maximum in the rate of polymerization so that it was close to the fastest observable rate (pH 2.2) in Figure 1. However, the fractional ionization significantly influenced the polymerization kinetics even at high ionic strengths, as a decrease was observed in the rate maximum as the pH was increased from 4.7 to 5.1 at constant ionic strength.

Kinetic Constants. The kinetic constants for propagation and termination were quantified using the after-effect experiments described in the experimental methods. In the absence of initiation, radicals are consumed only by termination, and integration of the radical species balance, assuming bimolecular termination, yields

$$\frac{1}{R_p} = \frac{2k_t t}{k_p[M]} + \frac{1}{R_{po}} \tag{1}$$

Here, R_p is the time-dependent rate of polymerization and R_{po} is the rate of polymerization at the instant that initiation is stopped (the UV light source is turned off). The term [M] is the molar concentration of monomer, t is time, and k_p and k_t are the propagation and termination kinetic constants, respectively. Hence, by plotting $1/R_p$ vs t, the ratio of k_t/k_p was determined. The rate constants were decoupled using an independent equation, obtained by applying the classical rate expression

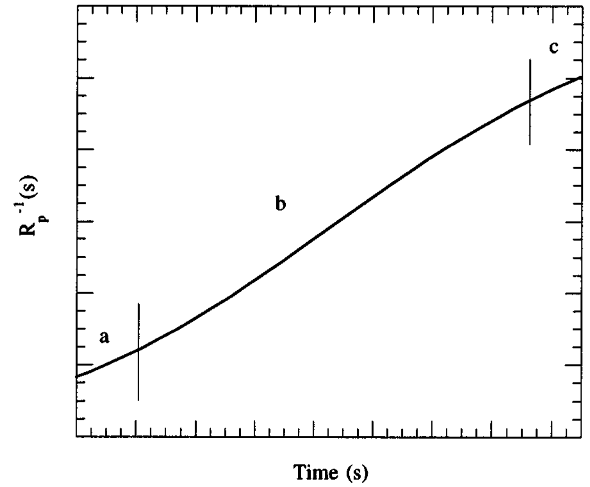


Figure 4. Representative plot of the inverse of the AA polymerization rate, R_p^{-1}, as a function of time in the dark. The slope in region b was used to calculate k_t/k_p.

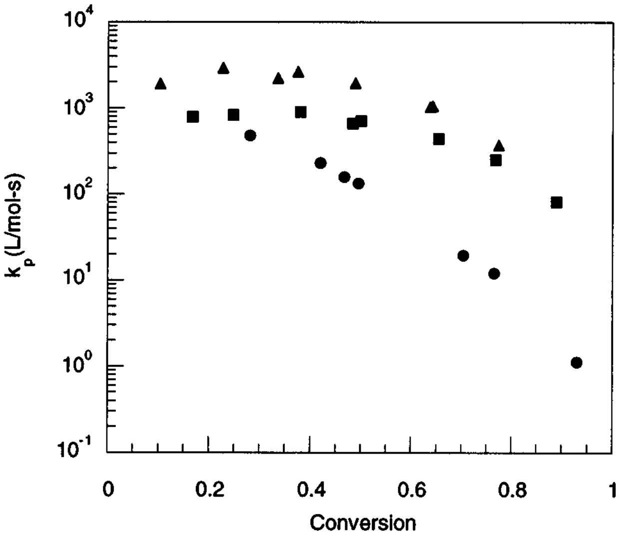


Figure 5. Propagation kinetic constant, k_p, as a function of conversion during the polymerization of 30 wt % AA solutions at pH 2.2 (▲), pH 4.7 (■), and pH 6.5 (●).

for radical photopolymerization:[16]

$$R_p = k_p[M]\left(\frac{\phi I_a}{k_t}\right)^{1/2} \tag{2}$$

I_a is the absorbed light intensity, and ϕ is the initiator efficiency. This gave the value $\phi k_p/k_t^{1/2}$. No attempts were made to measure ϕ, so this term was lumped together with the reported values of k_p and k_t. This analysis relies on the assumption that the kinetic constants are relatively constant over the time increment in the absence of initiation, where conversion changes are rather small (<2%).

Figure 4 shows a typical plot for the after-effect experiments. During the first 2–3 s after initiation has stopped (region a), the changes in the polymerization rate occurred faster than the DPC response time. In contrast, in region c (after 20–30 s), the magnitude of the polymerization rate was so low that monitoring the changes in rate was beyond the sensitivity of the DPC equipment. Thus, the data in region b was fitted to a line and used to determine the ratio k_t/k_p.

In Figure 5, k_p is plotted as a function of conversion at pH values of 2.2, 4.7, and 6.5. The k_p calculated was actually the average over all of the reacting species:

$$k_p = \sum_{i=1,2}\sum_{j=1,2} k_{p,ij}\phi_i\Omega_j \tag{3}$$

Here, ϕ_1 represents the fraction of non-ionized monomer, and ϕ_2 represents the fraction of ionized monomer. The terms Ω_1 and Ω_2 represent the fractions of non-ionized and ionized reactive macroradical sites, respectively. This treatment neglects ion pairing effects[9] and also the effects of monomer dimerization.[17] Each of these phenomena might contribute independently to the overall k_p value, with weightings corresponding to the relative concentrations of ion pairs and acid dimers. In general, the propagation kinetic constant for reaction between two uncharged species, $k_{p,11}$, was assumed to be greater than that for a reaction between a charged and an uncharged species, $k_{p,12}$ or $k_{p,21}$. The propagation kinetic constant for a reaction between two charged species, $k_{p,22}$, was assumed to be smallest. As the solution pH was varied, ϕ_i and Ω_j changed dramatically, while $k_{p,ij}$ remained relatively constant.

Several features related to the polymerization mechanism are apparent from the results of Figure 5. First, a marked decrease in k_p was observed at higher double bond conversions in each of the systems studied. For the pH 2.2 and pH 4.7 solutions, this decrease occurred between 70 and 80% conversion and ultimately led to a 1 order of magnitude decrease in k_p. In contrast, the pH 6.5 solution exhibited an earlier onset of the decrease, between 50 and 60% conversion, and k_p changed by nearly 3 orders of magnitude. These polymerizations were conducted at AA concentrations of approximately 30 wt %, and the final polymers were highly swollen gels.

The dependence of the apparent propagation kinetic constant on conversion (typically indicating diffusion control of the reaction) was not expected for these systems, but might be attributed to one of several causes. First, chain transfer during polymerization and/or dimerization of the monomer could have led to significant cross-linking, which would limit the mobility of reacting species and cause a decrease in k_p with increasing conversion.[18] Also, nonconstant pH or pK_a values over the course of polymerization would lead to conversion-dependent values of mole fractions ϕ_i and Ω_j. This would lead to conversion-dependent kinetics, according to eq 3. Kabanov *et al.*[10] have reported upward shifts of more than 2 units in the effective pK_a for polyacids in the presence of monomer molecules. Hence, as the polymerization proceeded (and monomer molecules were consumed), the pK_a of the polymer might have decreased substantially. Such a change in pK_a would lead to a reduction in k_p since $k_{p,22}$ is generally significantly lower than $k_{p,11}$, $k_{p,12}$, or $k_{p,21}$. Finally, a third possible explanation for the conversion dependence of k_p could be a change in the initiator efficiency.[19] Since the initiator efficiency was lumped into the measured kinetic constants, any change in the system that caused ϕ to drop would lead to a decrease in the measured values of both k_p and k_t.

In addition to the dependence of the apparent propagation kinetic constant on conversion, Figure 5 shows the dependence of k_p on solution pH. First, at low conversions (where k_p is relatively constant in each system), it was observed that k_p (pH 2.2) > k_p(pH 4.7) > k_p(pH 6.5). The figure shows that k_p decreased nearly 5-fold from pH 2.2 to pH 6.5.

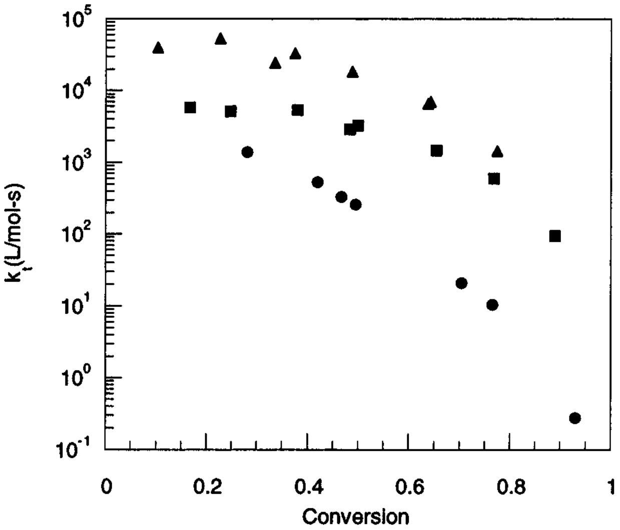


Figure 6. Termination kinetic constant, k_t, as a function of conversion during the polymerization of 30 wt % AA solutions at pH 2.2 (▲), pH 4.7 (■), and pH 6.5 (●).

The termination constant, k_t, was plotted as a function of monomer conversion at the same pH values discussed above, as shown in Figure 6. The calculated k_t was an average given by

$$k_t = \sum_{i=1,2}\sum_{j=1,2} k_{t,ij}\Omega_i\Omega_j \tag{4}$$

where the symbols and subscripts have the same definitions as previously described. The termination kinetic constant, k_t, decreased with conversion in each of the systems studied. However, the decrease occurred at much lower conversions than for k_p. At pH 2.2 and pH 4.7, k_t began to decrease significantly between 50 and 60% conversion, whereas near 100% conversion it had decreased almost 3 orders of magnitude. At pH 6.5, k_t had decreased already between 30 and 40% conversion, whereas at 100% conversion it was nearly 4−5 orders of magnitude lower than the initial value. Again, this dependence of k_t on conversion might be the result of either diffusion-controlled termination reactions or changes in the pK_a of PAA with conversion. Either of these explanations would also account for the earlier onset of the decrease in k_t compared to that observed for k_p. As in the case of k_p, a decrease in ϕ might also account for the conversion dependence of k_t observed in Figure 6. The figure also shows that k_t decreased by more than 1 order of magnitude as the pH was varied.

The values of k_p and k_t at low double bond conversions are plotted as a function of pH over the pH range 2.2−9.9 in Figure 7. In general, the plots can be divided into two separate regions. Between pH 2.2 and pH 6.2, the concentration of charged species and the ionic strength increased as a function of pH. These two factors had opposite effects on the polymerization rate and the effective kinetic constants. However, the ionic strength was relatively low, and the concentration of charged species was sufficiently high that an overall decrease in both kinetic constants was observed in this region. In the pH region above pH 6.2, however, the fractional ionization remained almost constant, and increasing the pH led only to an increase in the ionic strength of the solution. Thus, an increase in both k_p and k_t was observed, as the higher concentration of sodium counterions led to increased shielding effects and to an enhancement in the rates of both propagation and termination reactions.

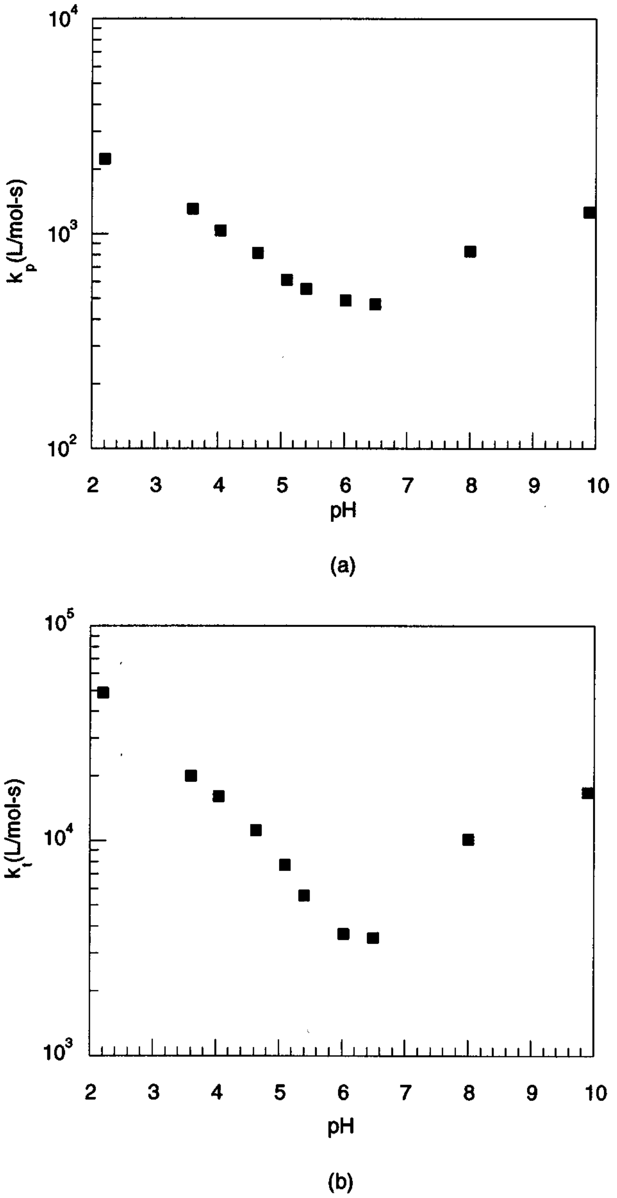
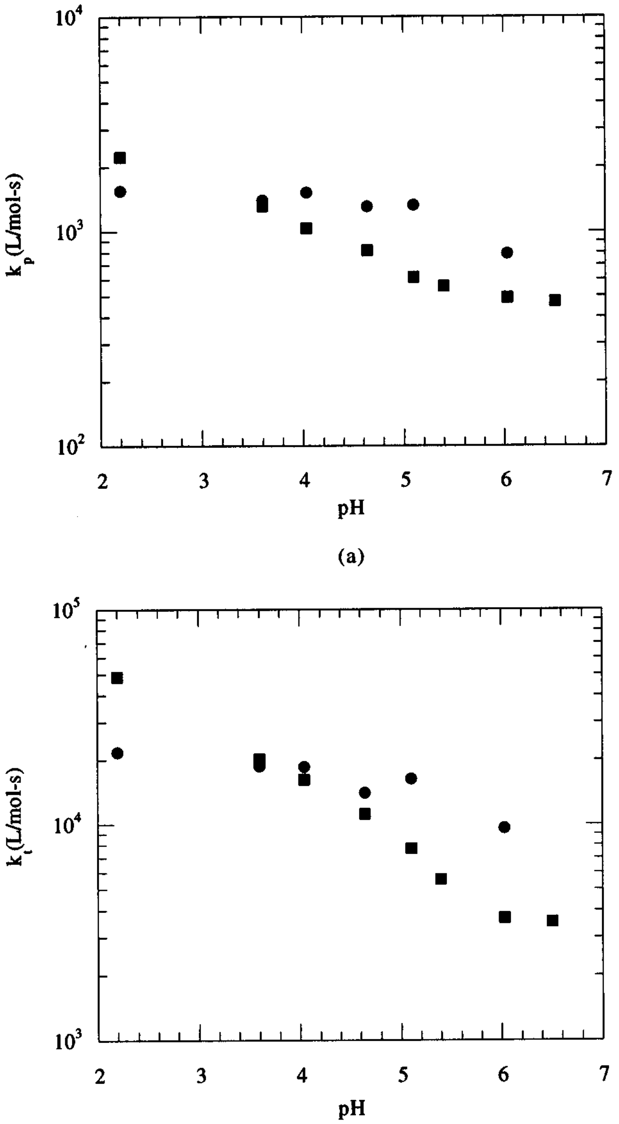


Figure 7. Kinetic constants, k_p (a) and k_t (b), as a function of pH during the polymerization of 30 wt % AA solutions.

To identify the relative contributions of ionic strength effects and ionization effects, the kinetic constants were also investigated at constant ionic strength for pH values ranging from 2.2 to 6.4. The ionic strength of each solution was kept constant by the addition of NaCl until the ionic strength of the given solution was equal to that of the pH 6.4 solution. The results from these experiments are shown in Figure 8, where k_p and k_t are plotted as functions of pH and compared to the data obtained under conditions of variable ionic strength. The figure shows that at low pH values the counterion concentration was sufficiently high to shield repulsion of charged reactants, and the kinetic constants remained relatively unchanged. However, beyond a pH value of 5, the extent of ionization became sufficiently high that electrostatic repulsion led to a lowering of the effective kinetic constants. This behavior was observed for both k_p and k_t.

Conclusions

The AA polymerization behavior and kinetics were investigated using differential photocalorimetry. The polymerization rate was strongly dependent on the



(a)

(b)

Figure 8. Kinetic constants, k_p (a) and k_t (b), as a function of pH during the polymerization of 30 wt % AA solutions under conditions of constant (●) and variable (■) ionic strength.

fractional ionization of the AA monomer and on the ionic strength of the solution. As the pH was increased from 2.2 to 6.5, the maximum rate of polymerization decreased by nearly 1 order of magnitude. Beyond pH 6.5, further increases in solution pH enhanced the polymerization rate because of ionic strength effects. To further elucidate the relative role of these contributing factors, the propagation and termination kinetic constants were also calculated as functions of conversion, pH, and ionic strength conditions.

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