

Absolute Online Monitoring of Acrylic Acid Polymerization and the Effect of Salt and pH on Reaction Kinetics

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ABSTRACT: Using recently introduced Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP), the kinetics of acrylic acid polymerization was studied. ACOMP yields the absolute weight-averaged mass (M_w), monomer conversion, and other quantities. As the initiator concentration increased, it was shown that the rate increased and the M_w decreased as in regular free-radical polymerization. The effect of salt on acrylic acid polymerization in an aqueous solution was investigated. The polymerization rate and M_w both decreased with an increasing salt concentration. ACOMP molecular weights were also compared with size-exclusion chromatography on aliquots periodically withdrawn during the reaction, and good agreement was found. The effect of the pH on the rate and

the molecular weight was also investigated, and when the medium pH was changed from 2 to 5 with sodium hydroxide, the rate and M_w both decreased as the pH increased. Light-scattering results of reaction end products in the reference solvent showed that molecules synthesized at higher pH were in a more expanded form. When equimolar sodium hydroxide was added to the acrylic acid (pH \cong 5) and sodium acrylate formed, adding salt did not effect the reaction kinetics of the poly(sodium acrylate); its effect on the products was a relatively minor decrease of M_w . © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1352–1359, 2004

Key words: light scattering; on-line monitoring; polymerization kinetics; poly(acrylic acid); poly(sodium acrylate)

INTRODUCTION

Poly(acrylic acid) (PAAc) is a water-soluble polymer. Due to its wide range of solubility in water and its polyelectrolyte nature, it is used in adhesives, flocculants, rubber emulsions, ion-exchange resins, and secondary recovery of oil.

The aims of this work were (1) to extend the recently introduced Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP) technique¹ to the case of PAAc and (2) to use the method to study the effects of the initiator, salt concentration, and pH on the polymerization kinetics and molecular weight of the products.

The polymerization of acrylic acid (AAc) was performed via a free-radical polymerization. The AAc monomer bears one elementary charge in an aqueous

solution, and it is expected that the details of the polymerization reaction in an aqueous solution will depend on the degree of ionic shielding. It might seem, at first, that as the salt concentration increases it would be easier, due to electrostatic shielding, to link negatively charged AAc monomers onto a growing polyelectrolyte chain. In fact, polymerization conducted at lower salt concentrations takes place at a higher rate and results in a higher molecular weight material.

Typical AAc concentrations during polymerization were 0.06 g/mL, which amounts to 0.833M of ionic strength. This is a very high ionic strength, so added salt is not expected to significantly alter the already high ionic shielding of the solution, but might influence equilibrium conditions.

When the amount of NaOH, that is, the pH, is changed, a decrease was observed both in the reaction rate and the molecular weight as the pH was increased. When AAc was neutralized by adding an equimolar amount of NaOH, the rate of the reaction and the molecular weight were not affected significantly by the extra added salt.

On-line monitoring of the kinetics and weights during the polymerization reaction provides an ideal tool for studying these effects. ACOMP furnishes the time-dependent signature of the cumulative weight-average

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mass M_w and the monomer conversion. More recently, several approaches have been taken to determine the evolution of the polydispersity during online monitoring.² ACOMP was used for the case of free-radical polymerization of acrylamide,³ of a polyurethane stepwise reaction,⁴ of a free-radical copolymerization reaction,⁵ to determine chain-transfer kinetics,⁶ in continuous reactor monitoring,⁷ and for controlled radical polymerization.⁸ The aim of the current work was to explore the kinetic ramifications of AAc polymerizations gathered by online monitoring. It is thought that ACOMP will provide new opportunities for the critical assessment of models for polymerization kinetics, as well as useful tools for the practical control of polymerization reactions.

EXPERIMENTAL

Online monitoring of polymerization reactions

ACOMP was described in detail in refs. 1–3. Briefly, it relies on the automatic, continuous withdrawal of a small stream of a reactor solution, which is continuously mixed with a pure solvent from a reservoir, to produce a very dilute polymer solution, on which absolute light scattering and other measurements can be made. An ISCO 2360 programmable mixer was used to continuously withdraw nominal, preset percentages from the reactor and solvent reservoir, set at 4 and 96%, respectively. The flow rate was 2 mL/min, so that about 5 mL of the reactor solution was consumed during the course of a typical reaction.

The diluted solution was continuously pumped through a detector train consisting of (1) a home-built, seven-angle absolute scattering intensity monitor for time-dependent static light scattering (TDSLS), details of which have been recently published,^{1,9} (2) a Shimadzu SPD-10AV ultraviolet (UV) absorption spectrophotometer, with a 0.01-cm path-length cell monitoring UV absorption at 260 and 265 nm, and (3) a Waters 410 differential refractive index (RI) detector. The UV and the RI detector signals, plus the fact that the total monomer plus polymer concentration in the reactor is constant, provide three equations, which yield the instantaneous concentration of a polymer and monomer in the detector stream as long as the refractive index increment dn/dc is known for both the monomer and the polymer. The dn/dc values and the ultraviolet absorption response dUV/dc of the polymer, monomer, salt, and initiator are given in Table I.

In conjunction with the polymer concentration c , determined in the following way, the multiangle TDSLS monitor allows computation of the absolute M_w and $\langle S^2 \rangle_z$, using the well-known Zimm approximation,¹⁰ valid for $q^2 \langle S^2 \rangle_z \ll 1$:

TABLE I
Values of dn/dc and dUV/dc for AAc, poly (AAc), Salt, and Initiator

Material	dn/dc (cm^3/g)	dUV/dc (265 nm) ($\text{V cm}^3/\text{g}^{-1}$)	dUV/dc (260 nm) ($\text{volt cm}^3/\text{g}^{-1}$)	A_2 (cm^3 mol g^{-2})
AAc	0.1228	166.78	262.57	—
PAAc	0.1496	0	0	7.423e-5
KBr	0.1222	0	0	—
Persulfate	0.016	29.21	39.56	—

$$\frac{Kc}{I(q,c)} = \frac{1}{M_w} \left(1 + \frac{q^2 \langle S^2 \rangle_z}{3} \right) + 2A_2c \quad (1)$$

where $I(q,c)$ is the excess Rayleigh scattering ratio (total scattering of a polymer in a solvent minus the scattering level), and K is an optical constant, given for vertically polarized incident light by

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \quad (2)$$

where n is the solvent index of refraction; λ , the vacuum wavelength of the incident light; and q , the usual scattering wave vector $q = (4\pi n/\lambda) \sin(\theta/2)$, where θ is the scattering angle.

The second virial coefficient, A_2 , was determined independently in separate light-scattering experiments on the final products. Zimm plots gave $7.035 \times 10^{-5} \text{ cm}^3 \text{ mol/g}^2$ for PAAc synthesized at pH 2.5 and measured at a 0.1M ionic strength. Hence, determination of $I(q,c)$ and c at every point in time allows M_w to be computed from the above equation. The temperature inside the reactor was monitored continuously with a k -type thermocouple.

Potassium persulfate-initiated AAc polymerization

AAc, potassium persulfate (hereafter persulfate), and potassium bromide were from Aldrich. The chemicals were used as received. Water was deionized and filtered by a 0.22- μm filter in a Millipore Modulab UF/UV system. In the polymerization experiments, the AAc solution was placed in a glass reactor and degassed for 30 min by N_2 bubbling. The thermocouple and Teflon sampling tube were inserted into the reactor and then the system was placed in a water bath stabilized at 60°C. The solution was magnetically stirred throughout the reaction.

An HPLC mixing pump was used to continuously withdraw nominally 4% of the liquid from the reaction vessel and mix this with a 96% 0.1M KBr solution from the reservoir. Thus, the salt concentration in the detector train is determined by the concentration in

TABLE II
Persulfate-initiated AAc Polymerization at 60°C with the Carrier Solution Being a 0.1M KBr Solution in All of the Following Experiments

Experiment no.	AAc (g) 0.83M [g (AAc)/g (w)]	Persulfate [g (per)/g (w)]	Added salt [g (salt)/g (w)]	Initial rate $\times 10^{-4}$ (s ⁻¹)	Final M _w
P-I (dn/dc exp)	0.03915	0.003221 powder	—	—	—
P-II	0.06048	0.003611	—	9.9	370,000
P-III	0.05972	0.008005	—	18.0	198,000
P-IV	0.05998	0.013953	—	24.0	186,000
P-V	0.06016	0.003630	0.001174 (0.01M)	10.0	370,000
P-VI	0.06026	0.003618	0.005911 (0.05M)	8.9	310,000
P-VII	0.06020	0.003613	0.03552 (0.3M)	6.7	150,000
P-VIII (SEC exp)	0.06563	0.003918	0.01M KBr	—	—

the carrier solvent so that it was not necessary to recalibrate the detectors for experiments at different salt concentrations. The diluted solution flowed continuously through the detectors, which were stabilized before the initiator was added. After stabilization, a 2 mL persulfate solution in degassed water was added to the reaction. The reaction conditions for different experiments are given in Table II. The conversion of the monomer to polymer was followed with the UV detector set at 260 and 265 nm (double wavelength mode). Aliquots were withdrawn during the reaction P-VIII and their molecular weights were measured by gel permeation chromatography (GPC) and compared with the on-line measured data.

dn/dc determination experiment for AAc

The differential refractive index of a polymer in a solvent is not necessarily equal to that of its monomer. For this reason, it must be determined experimentally. The dn/dc values of the monomers and the corresponding polymers were measured by a previously described technique.¹¹ The differential refractive indices of the AAc and its polymer, PAAc, obtained by manipulation of the data from Figure 1, were found as 0.1228 and 0.1496, respectively (reaction P-I). These values were assumed to change insignificantly at different pH values, consistent with the authors' previous experience with polyelectrolytes in varying pH and ionic strength conditions.

In Figure 1, the decrease in the UV signal directly monitors AAc conversion, whereas the increase in the RI signal shows that the dn/dc of the polymer is measurably higher than for AAc. The step signals between 6000 and 7000 s show the effect of persulfate, at the concentration used in the reaction, on the UV and RI signals, so that they can be subtracted when computing dn/dc for AAc and PAAc.

pH dependence of AAc polymerization

In another group of experiments (Table III), the pH of the AAc solution was changed by adding different amounts of sodium hydroxide and polymerized using 4,4'-azobis(4-cyanovaleric acid) (ACV) as the initiator. The above procedure is followed and the only difference is that the initiator is added as a solid at 70°C. The details of the experiment are described above.

Salt effect in sodium acrylate polymerization

The equimolar sodium hydroxide added to AAc, the acid and sodium hydroxide amounts, and the pH values are given in Table IV. The temperature was 70°C. In a series of experiments, KBr was added into the reaction in different amounts to determine the salt effect during the reaction.

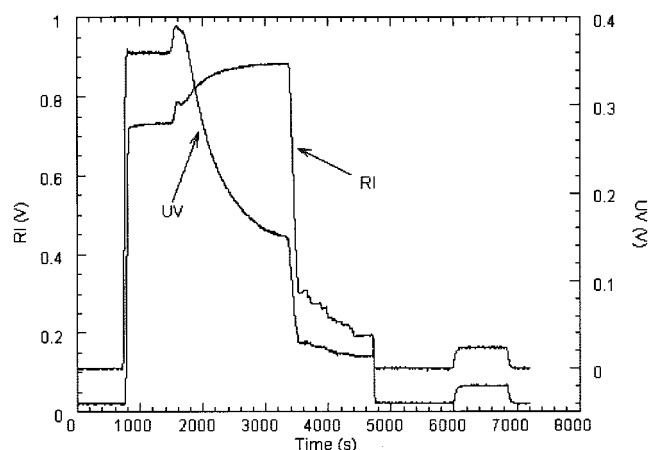


Figure 1 Raw data for the dn/dc experiment (P-I) for AAc. The abrupt decrease in detector signals at $t = 3400$ s is when the sample stream from the reactor is cut off and pure solvent flows, in anticipation of making the pure initiator response measurements at $t = 6000$ s.

TABLE III
AAc Polymerization at Different pH Values (at 70°C, ACV Initiated)

Experiment no.	AAc (g) 0.83 M	NaOH (g)	Water (g)	ACV (g)	pH (0)/ pH (fin)	Initial rate $\times 10^4$ (s ⁻¹)	Final M_w (g/mol)
A-I	1.5052	0.7802 (0.73M)	25.015	0.1018	5.51/6.76	5.2	26,000
A-II	1.5083	0.1478 (0.14M)	25.0025	0.1016	3.57/4.10	9.5	91,000
A-III	1.5018	0.0080 (0.008M)	25.0237	0.1017	2.53/2.51	14.5	198,000

RESULTS AND DISCUSSION

Persulfate-initiated AAc polymerization

Table II is a summary of all potassium persulfate-initiated AAc polymerizations, with different amounts of persulfate and salt concentrations. Figure 2 shows the monomer conversion f ($f = 1 - [m]/[m]_0$) versus the reactor time for different initiator concentrations. The curves in Figure 2 can be treated approximately as first order over a significant portion of the reaction. The initial rates are given in the sixth column of Table II. As expected, the rate increased with an increasing initiator concentration.

Figure 3 shows the molecular weight versus time. The general trend is that, at early times, large polymer chains are produced, and M_w decreases steadily as the conversion proceeds. This trend is consistent with ideal polymerization kinetics,¹²⁻¹⁴ since the monomer concentration is continually decreasing with the conversion. Previous online polymerization monitoring experiments gave similar results. During all (persulfate-initiated) AAc polymerization reactions, the pH of the medium was around 2.5, which means 98% acid in nonionized form and the chains were preferably in a coiled form at pH 2.5. The final molecular weight values are given in the last column in Table II. As expected, the molecular weight decreased with an increasing initiator concentration. The insets to Figures 2 and 3 show the initial polymerization rate versus $\sqrt{[I]}$ and the final M_w versus $1/\sqrt{[I]}$. The results are roughly linear, consistent with ideal polymerization.

The monomer concentration (0.8M) gives an ionic strength that is far beyond the polyelectrolyte regime where polyelectrolyte conformations and interactions are steeply sensitive to low to moderate ionic strength.^{15,18} At such a high concentration, the added salt (0.01–0.3M) has only a minor effect on the ionic

strength of the solution. However, the added salt reduced the solvent quality appreciably and the decrease in the solvent quality is clearly observed in the molecular weight evolution, shown in Figure 4. When the amount of salt increased to 0.3M, the molecular weight dropped to half of the nonsalted weight. The initial rates and the final molecular weights are given in Table II. The inset to Figure 4 shows the decrease of both the polymerization rate and the molecular weight with an increasing salt concentration. Note that the M_w decreases much more steeply. Since the overall polymerization rate is the product of the kinetic chain length and the initiation rate, this phenomenon can be explained by the presence of salt increasing the initiation efficiency but more than compensating for this by suppressing the propagation reaction.

Because ACOMP has only recently been introduced, it is prudent to continue to substantiate its validity with respect to traditional equilibrium characterization techniques. Hence, Figure 5 shows the values of M_w from size-exclusion chromatography (SEC) for aliquots that were, periodically, manually withdrawn during reaction P-VIII, superposed on the online data. The SEC system used has been previously described.¹⁹ The values obtained for M_w from the two independent techniques are very close.

Effect of pH on AAc polymerization

Experiments with ACV were performed at different pH values, given in Table III, by adding NaOH to the reaction medium. The ionization degree increased from 2 to 98% as the pH was increased from 2.5 to 5.5.

When the medium pH is changed by the addition of NaOH, both the rate and molecular weight were affected strongly. The rates (R_p) are computed from the curves of monomer conversion versus time in Figure 6. The molecular weights given in Figure 7 show that

TABLE IV
Sodium Acrylate /ACV-initiated Experiments With and Without Added Salt, at 70°C and pH 5.67–5.51

Experiment no.	AAc g (AAc)/g (w)	NaOH g (AAc)/g (w)	ACV g (ACV)/g (w)	Added salt KBr (mg)	pH	Initial rate $\times 10^4$ (s ⁻¹)	Final M_w
A-I	0.06016	0.03119	0.004070	0.0	5.51	6.9	27,000
A-IV	0.05983	0.03189	0.004043	0.298	5.63	6.8	18,000
A-V	0.06536	0.03235	0.004038	7.149	5.67	6.6	18,000

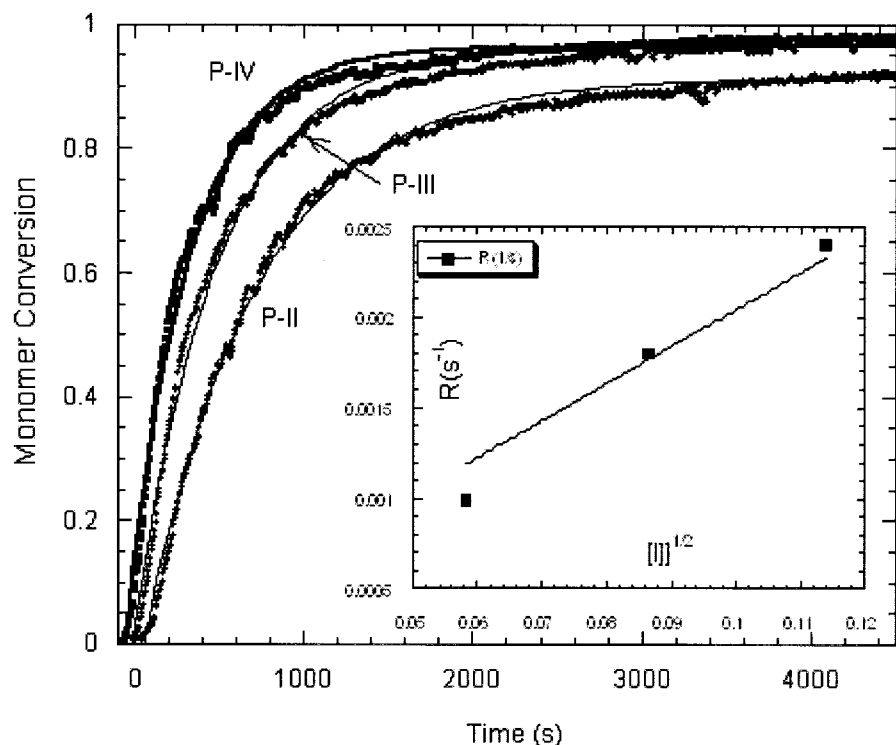


Figure 2 Effect of initiator concentration on rate of AAC polymerization. Plots are (top to bottom) experiments P-IV, P-III, and P-II, respectively. First-order kinetic fits are also shown. The inset to Figure 2 shows the initial rate plotted versus $[I]^{1/2}$.

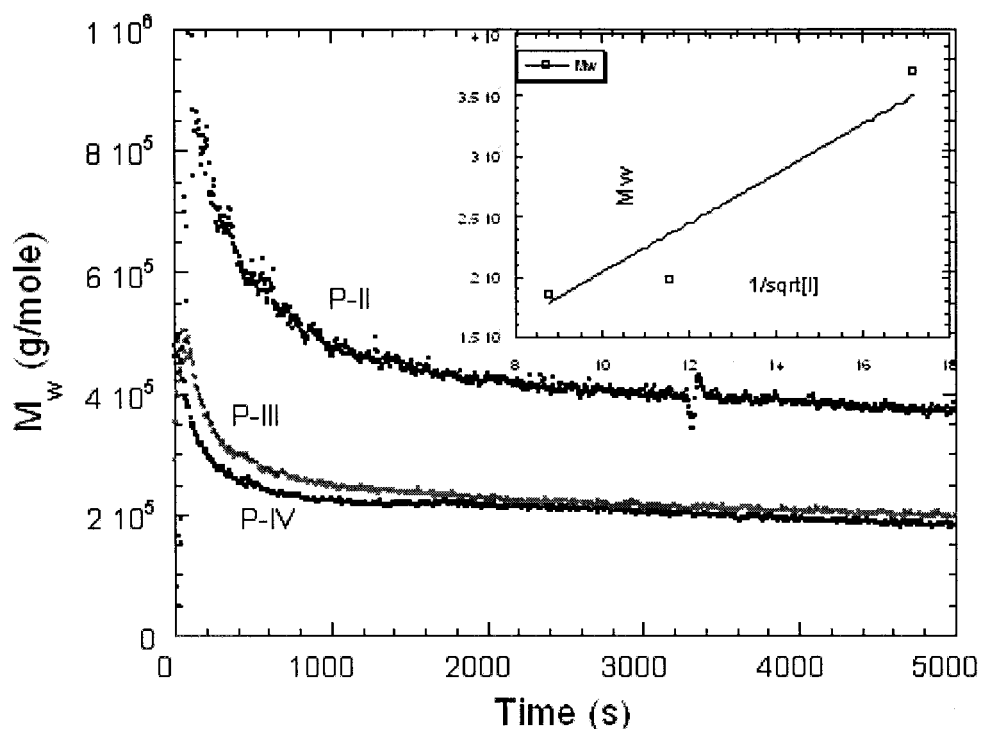


Figure 3 Effect of initiator concentration on corrected molecular weight versus time in AAC polymerization. Experiments P-II, P-III, and P-IV are shown from top to bottom. In the inset, M_w is plotted versus $1/[I]^{1/2}$ for the experiments mentioned above.

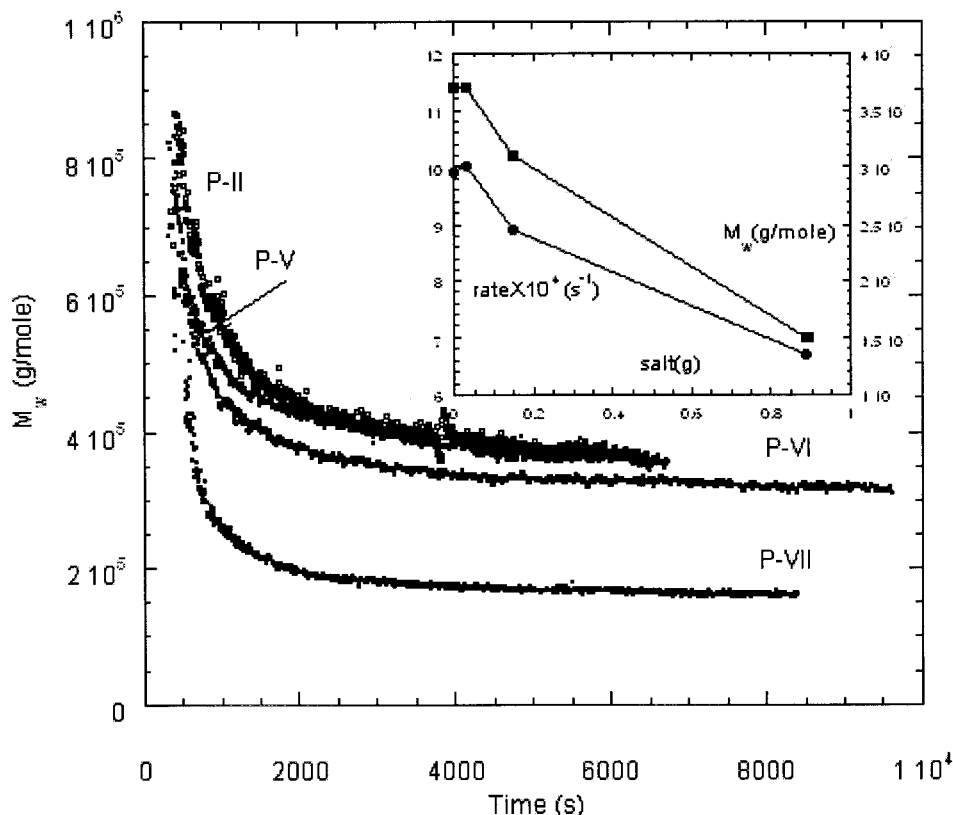


Figure 4 Effect of salt on molecular weight evolution in AAc polymerization. (M_w versus time). Reaction P-II is salt free, and reactions P-V, P-VI, and P-VII contain increasing amounts of salt, given in Table II. The inset to Figure 4 shows the molecular weight and polymerization rate versus the salt concentration (pHB2.5).

both R_p and M_w increase monotonically with increasing acidity. The values for the rates and the final molecular weights are given Table III. Kabanov et al. studied the pH dependence of AAc polymerization and found that as the pH increased from 2.5 to 5.5 the

rate decreased three times.²⁰ This work corroborates the quoted kinetic results and also provides M_w data.

The M_w results rule out the possibility of the rate increase being primarily due to initiator efficiency ef-

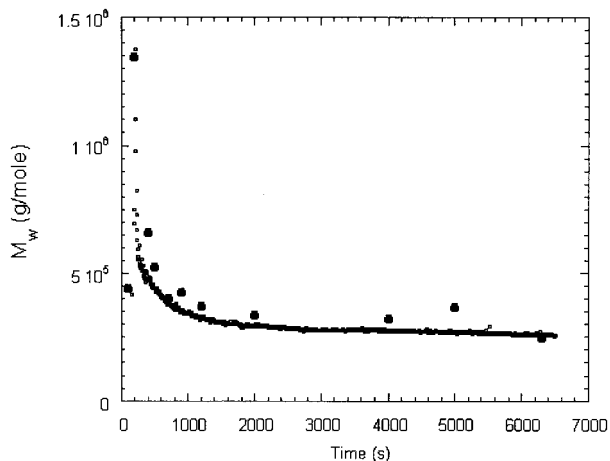


Figure 5 M_w versus conversion for both discrete SEC points (withdrawn periodically and manually from reaction P-VIII), represented by the large circles.

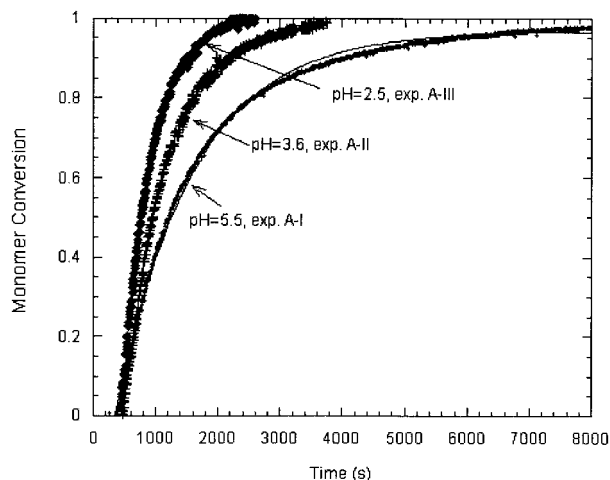


Figure 6 Effect of pH on the rate of AAc polymerization. Experiment A-I at initial pH 5.5 is the bottom plot; A-II at pH 3.6, the middle plot; and A-III at pH 2.5, the top plot. First-order kinetic fits are also shown.

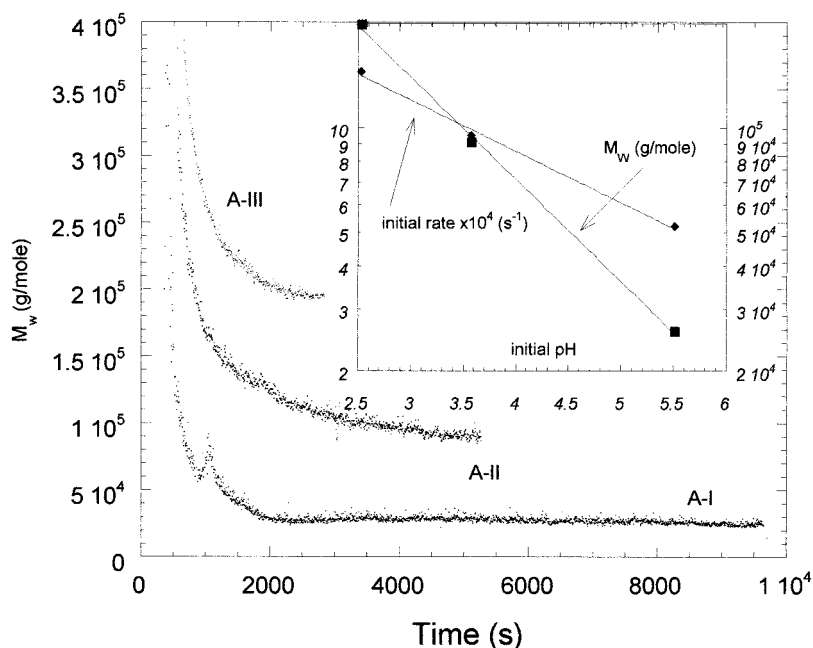


Figure 7 Effect of pH on molecular weight versus time in sodium acrylate polymerization. Experiment A-I is the bottom plot; A-II, the middle; and A-III, the top. Shown in the inset to this figure is the pH effect on the rate and the molecular weight.

fects. The increase in both R_p and M_w indicates that the ratio of the propagation and termination rate constants ($k_p/\sqrt{k_t}$) increases with the acidity of the medium. The inset to Figure 7 shows that both R_p and M_w decrease exponentially with the pH. Since the M_w decrease is faster ($M_w \propto R_p^{1.98}$), we can again state that the initiator efficiency increases with an increasing pH but this is more than compensated by the decrease of the chain length. A possible mechanism here is the increased rigidity of the chain caused by the higher degree of ionization at higher pH, slowing the reaction. Since the fraction of monomers and monomeric units in the macroradicals which are in ionized form increase with an increasing pH, electrostatic repulsion between the monomers and macroradicals can suppress the propagation reaction at higher pH values.

Effect of salt concentration on sodium acrylate polymerization

In this series of experiments (A-I, A-IV, A-V), sodium acrylate was polymerized at pH 5.5 with KBr salt added at different concentrations to the reaction medium. In this case, the added salt did not affect the rate of polymerization; the initial rates are given in Table IV, and only a slight change was observed at this pH. However, the added salt reduced the solvent quality and decreased the molecular weight; the final molecular weight values are also given in Table IV. The molecular weights in these experiments are low and show considerable scatter. For this reason, it is not

possible to draw a conclusion on whether a chain-transfer-type activity is involved.

CONCLUSIONS

ACOMP studies of AAc polymerization yielded several results: Salt-free reactions performed at pH 2.5 are consistent with ideal polymerization, both in the kinetics and in the evolution of the M_w . The addition of either salt (KBr) or base (NaOH) decreased both the M_w and the R_p . This decrease is not due to a suppression of the initiation because the chain-number concentration is actually higher in the high salt and high pH reactions, since the decrease in M_w is more significant than is the decrease in the R_p . It is the propagation step that is suppressed. This suppression can be due to either the reduction of the solvent quality or a retardation (in the Bamford sense¹⁴) and chain-transfer activity of the ions. The latter could be the case if the activity is transferred to an ion, which then is slow to reinitialize or fails to reinitialize. Alternately, the effect of salt might be due to hindrance caused by the ions and their water shells and that of higher pH due to increased rigidity of chains caused by a higher degree of ionization. ACOMP should prove to be a useful technique both for a more in-depth study of PAAc and its copolymers and also as a potential means for feedback control in industrial-scale reactors.

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