Polyacrylic Acid (Poly-A) as a Chelant and Dispersant

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ABSTRACT: Polyacrylic acid was synthesized in water by persulfate-initiated polymerization (solution polymerization) of glacial acrylic acid in the absence of a chain-transfer agent. The final product is odorless and colorless. Chelation for calcium ions using a calcium electrode show that our poly(acrylic acid) has a higher chelation capacity than that of existing commercial poly(acrylic acids). A design of experiments was performed to optimize the synthesis conditions to obtain poly(acrylic acid) with a high maximum chelation value. These studies also helped us to gain insight into its high chelation capacity. The chelation capacity for calcium reaches its highest values when polymerization near isothermal conditions is done $\sim 95^\circ\mathrm{C}$ with an acrylic acid concentration of \leq 21 wt % and an addition time >1 h. These conditions favor higher molecular weight poly(acrylic acid) with a polydispersity \sim 4. The dispersion properties of our poly(acrylic acid) are similar to those of the commercial ones. This dual capability of chelation and dispersion is absent in commercial chelants such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and their analogs. At pH > 7, chelation of calcium by our poly(acrylic acid) is much higher than that observed with EDTA. Characterization by NMR, Raman, FTIR, and molecular modeling are included in an attempt to understand structural features that can explain the higher chelation capacity of our atactic poly(acrylic acid). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1097-1115, 1999

Key words: Poly (acrylic acid); chelant; dispersant; polymerization; acrylic acid; free radical

INTRODUCTION

Growing social awareness and concern for the quality of the environment and the state of our natural waters have been the major driving force to search for detergent additives other than phosphates. Of all of the 20 chemical elements essential for the growth of algae, phosphorus was accused as being responsible for eutrophication.^{1–3} Household detergents are one of the sources for phosphates.³ Many countries have passed legisla-

tion to reduce the phosphate content of their products without reducing the level of performance expected by the customers. Thus, the incentive to replace phosphates in the detergent industry led to the synthesis of poly(acrylic acid) (Poly-A) with a high chelation capacity for calcium.^{4,5}

Recent interest in Poly-A resurfaced due to potential market attractiveness on the use of Poly-A as a Ca^{2+} chelant to compete with commercial chelants. Poly-A is an anionic polyelectrolyte⁶; besides its chelation ability, Poly-A has dispersion properties³ which are absent in the commercial chelants like ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and their analogs.⁷ Our interest in Poly-A is also related to its different applications. At

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present, polyacrylates are sold as superabsorbants, dispersants, detergent builders, and thickeners, as additives in hydraulic fluids and petroleum recovery liquids, as ion-exchange resins where a weak acid is desired, and as an adhesive.⁸

In this article, we describe the syntheses of Poly-A in the laboratory by persulfate-initiated polymerization of glacial acrylic acid in water. We used an experimental design to achieve the optimum conditions with high Ca^{2+} chelation. The current synthesis does not involve a chain-transfer agent (octanethiol) as used previously^{4,5}; thus, the final product is clear, colorless, and odorless. Further, we have characterized our Poly-A's by aqueous gel permeation chromatography (AGPC), FTIR, Raman, and NMR. Poly-A with molecular weights (M_w) in the range of 50,000–200,000 exhibits high chelation for Ca²⁺ at high pH in contrast to the commercial Poly-A's investigated in our laboratory. Our Poly-A's with molecular weights (M_w) in the range of 50,000–90,000 also show a high dispersion for ferric ions and good dispersion for CaCO₃.

EXPERIMENTAL

General

EDTA and sodium persulfate were purchased from Aldrich, Milwaukee, WI. Celanese glacial acrylic acid, >99+% pure, containing 200 ppm of monomethyl ether hydroquinone (MEHQ) was used as such in these polymerization experiments. The presence of MEHQ reduces the rate of polymerization but it does not affect the final molecular weight of the polymer.⁹ A simulated ester-grade acrylic acid was also used in the polymerization reaction. Ester grade was a stage of purification prior to glacial but good enough to be used as raw material available at low cost. The original ester-grade acrylic acid was simulated using the following mixture: glacial acrylic acid (92%), acetic acid (4.0%), propionic acid (0.2%), maleic acid (0.5%), ethyl acrylate (0.3%), and water (3.0%).4,5

Analysis of the free acrylic acid monomer at the end of the polymerization experiment was determined by GC (Hewlett Packard 5890) equipped with a capillary DB-FFAP column from J&W and a flame-ionization detector. A typical analysis of a Poly-A solution, prepared from a simulated estergrade acrylic acid, contains <1 wt % of acetic acid, 0.06% of propionic acid, and 0.34 wt % of acrylic acid. Poly-A solutions prepared from pure glacial acrylic acid contain <0.5 wt % of monomer in all cases. Thus, the conversion is extremely high in all cases. The amount of persulfate at the end of polymerization was measured to be <50 ppm using persulfate strip indicators by Quantofix (from Gallard-Schlesinger Industries, Inc. Carle Place, NY). These strips are capable of detecting as low as 5 ppm of persulfate. We tested them under our conditions (in the presence of Poly-A at pH \sim 2) to validate their responses. For experimental design, statistical analysis, including multiple regression, was conducted using a modeling and design software package (MODDE version 2.1, UmetriAB, Sweden).

Synthesis of Poly-A

Poly-A was synthesized in a 3-L, three-neck, round-bottom flask that was partially submerged in hot silicone oil. The oil was contained in a glass bell jar, 10 in. in diameter and 10 in. deep, wrapped in insulation to prevent heat loss and placed on a stirring hot plate. A stir bar placed in the silicone oil provided for even heating of the oil. A heating element placed in the oil and connected to a temperature controller was used to maintain the desired constant temperature inside the flask. In general, the procedure consisted of a load of 688 g of double-distilled water placed in the round-bottom flask fitted with an overhead stirrer and an 18-in. condenser. The pot temperature was typically maintained at 95–98°C. A digital thermometer was used to monitor the temperature of the silicone oil and reaction pot.

Two FMI LAB PUMPS, Model QVG 50, were used to meter in a 211.6 g of glacial acrylic acid (4.0 mL/min) and 60 mL of the initiator (1.0 mL/min)min). The amount of acrylic acid monomer varied in the range of 20% ($\sim 3.7M$) to 25% ($\sim 4.3M$) by weight during the experimental-design work. The initiator, sodium persulfate, was prepared by dissolving 2.50 g of solid in 57.5 g of water (this amount also varied during the experimental-design runs shown below in the section on statistical analysis). After the persulfate is delivered to the reactor, the concentration is $\sim 0.01M$. The acrylic acid and initiator were metered simultaneously over a 60-min period unless indicated otherwise (see Statistical Analysis of the Poly-A Process). The heating with slow stirring was continued for another 60 min. Temperature readings were recorded every 15 min during the 2-h run.

For those experiments that required temperatures >100°C, we used a 1-L Buchi glass reactor that was pressurized to 20-30 psig with N₂. After the reactions were completed (2 h), the reactor was cooled and vented and the Poly-A was removed.

Brookfield Viscometry

To determine the viscosity of the samples, a Brookfield viscometer was used. Two hundred fifty milliliters of Poly-A was poured into a 500-mL beaker. We used a Spindle 03, temperature set at 25°C, and the polymer viscosity read out was in centipoise.

Aqueous Gel Permeation Chromatography (AGPC)

AGPC was performed to determine the molar masses of Poly-A and their polydispersity. The gel permeation chromatograph was from Waters and equipped with a Waters 410 differential refractometer. The column bank consists of three Waters Ultrahydrogel columns: 250, 500, and 1000 Å. The samples were dissolved in the mobile phase at a concentration of 0.05 wt %. The mobile phase consisted of 2% methanol in water with a 0.05M ammonium acetate solution and adjusted to pH 7.2 with ammonium hydroxide. The mobile phase was then filtered with a $1.0-\mu$ filter and purged with helium before use. The flow rate, the column temperature, and the injection volume were 0.85 mL/min, 50°C, and 100 µL, respectively. The Poly-A standards, MW: 2000-500000, were obtained from Polysciences.

Chelation and Dispersion Experiments

The amount of Ca^{2+} chelated by the sequestrant was measured using a calcium-selective electrode. The procedure was described elsewhere.⁴ Blay and Ryland⁴ found that, at pH 9.5, the titration curve for chelation of Ca^{2+} by EDTA remains essentially constant, whereas the one corresponding to Poly-A is distinctly different. The chelation goes through a maximum and decreases thereafter with successive addition of Poly-A as shown in Figure 1. The chelation values are calculated on the basis of $CaCO_3$ (hardness):

$$CV = \frac{200 - (hardness left, mg/L)}{4 (chelant added, g)}$$
(1)

where 200 represents hardness in milligrams (expressed as $CaCO_3$) equivalent to 80 mg Ca^{2+} actually added as $CaCl_2$.⁴ The calcium-selective electrode from Orion (Model 93-20) is connected



Figure 1 Chelation value plot. Hardness level 200 mg CaCO₃; pH 9.2; 25°C.

to an Orion pH/ISE meter, Model 710A. The majority of the samples were run at pH 9.5. A key experimental response is the *maximum chelation value* (MCV), and it is obtained graphically by plotting percent chelation versus chelating values (mg CaCO₃/g Poly-A). Notice from Figure 1 that the maximum chelation value (MCV) is observed at a very low concentration of Poly-A and it corresponds to the maximum point of the plot.

Dispersion of calcium is demonstrated by the Hampshire test,³ which is generally accepted as the test method for encrustation inhibitors in the detergent industry. The procedure consists of dissolving 2 g of the product in 100 mL of distilled water. The acid solution is neutralized with NaOH. Then, 10 mL of a 2% Na₂CO₃ solution is added. After adjusting the pH to 11, the mixture is titrated with a 0.1M CaCl₂ solution until turbidity persists.

Dispersion values for Fe³⁺ are obtained by dissolving 10 g of the Poly-A solution (~ 20 wt % solids) in 500 mL of distilled water. Of this, 10 mL are taken into a series of six 150-mL beakers by a pipette and diluted with 80 mL of distilled water. To each beaker, different amounts of a Fe³⁺ standard solution (10 mg Fe³⁺/mL) are added. The pH of the solution in each case is adjusted to 9.5 using 0.1N NaOH. The solutions from the beakers are taken to six 250-mL round-bottom flasks and heated to reflux for 1 h. The flasks are allowed to cool to room temperature and the turbidity of the solutions are evaluated with a turbidimeter. The turbidity versus added mg Fe³⁺ is plotted. The plot will have two intersecting lines and the in-

Initiation	$S_2 O_8^{2-} \longrightarrow 2SO_4^+ (k_D \text{ often rate controlling})$
	$SO_4^+ + CH_2 = CHCOOH> SO_4 - CH_2 CH COOH (M_1)$
Propagation	a - M_1 · + M_2 ·> M_2 , b - M_2 · + M_2 ·> M_3 ·
	$\mathbf{c} - \mathbf{M}_{\mathbf{n}} + \mathbf{M} \mathbf{M}_{\mathbf{n}+1}$
Chain Transfer	a - Mn^{\cdot} + CT -H> Mn -H + CT^{\cdot} , b - CT^{\cdot} + M> CT -M.
Termination	$\mathbf{a} \cdot \mathbf{M}_{n} \cdot + \mathbf{M}_{n} \cdot \cdots \ge \mathbf{M}_{n} \cdot \mathbf{M}_{n} \cdot \mathbf{b} \cdot \mathbf{M}_{n} \cdot + \mathbf{M}_{n} \cdots \ge \mathbf{M}_{n} + \mathbf{M}_{n}$

Scheme 2	1
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tersection point corresponds to the amount of Fe^{3+} solubilized.

Statistical Analysis

An experimental 2^{4-1} resolution IV factorial design¹⁰ (see discussion) was used for our purposes and the following four factors were evaluated: glacial acrylic acid (200–230 g), initiator (persulfate, 2–6 g), addition rate (30–90 min), and applied temperature (80–100°C). The total mass in the reaction vessel was kept to an average of 980 g.

RESULTS AND DISCUSSION

General Aspects of the Polymerization Reaction and the Improved Poly-A Process

The Poly-A discussed in this article is produced by persulfate-initiated polymerization, also known as free-radical (or radical-chain) polymerization of acrylic acid in water. The mechanism for the polymerization is shown in Scheme 1.^{10,11} The use of persulfate as an initiator is well documented.^{11–14} Its major drawback is its lack of long-term stability in water^{15,16} which is reflected by a decrease in the number of growing chain radicals produced as the persulfate solution ages. Thus, to prevent decomposition of the initiator, fresh solutions of the persulfate were always prepared prior to polymerization.

We chose solution polymerization for multiple reasons: It provides several advantages over bulk polymerization: easy agitation, formation of longer polymer chains, and easy heat control.¹¹ The latter is very important since the polymerization of acrylic acid is exothermic. A serious disadvantage of solution polymerization is the participation of solvent in the chain-transfer steps, that is, the reaction with the solvent.^{10,11} However, in the present case, water does not undergo this kind of reaction to a great extent.¹¹

Glacial acrylic acid, used for polymerization, contains about 200 ppm of MEHQ which is an inhibitor and its ability to inhibit the polymerization of acrylic acid is directly related to the presence of oxygen.^{9,17,18} The inhibition effect is probably the result of oxidation of MEHQ to quinones¹⁷ which can also arise by persulfate (known as the Elbs reaction) that is present in the reaction mixture. However, Levy found that at 100°C, in the absence of oxygen, there is no induction time in the polymerization of acrylic acid in the presence of MEHQ.¹⁸ We performed an experiment in which the reaction vessel was continuously purged with N2 during the reaction. We did observe a very short induction period (ca. 2 min) at 95°C and the resulting polymer provided a similar MCV as the ones with no N₂ purge. Although there is no purging with nitrogen in most of our reactions, the reaction vessel is almost a closed system since all the openings are stoppered with the pump outputs, the reflux condenser, and the thermocouple. Therefore, the oxygen content in the vessel should be fairly constant or similar in all our reactions.

In the earlier stages of this work, we used ester-grade acrylic acid and octanethiol, a chaintransfer agent, in the polymerization reaction. In later runs, especially in our recent investigations, we replaced the ester-grade acrylic acid with the glacial acrylic acid and further eliminated octanethiol. The resulting polymers had similar chelation values for Ca²⁺ to the ones obtained with the chain-transfer agent and the ester-grade acrylic acid. This is a significant improvement of the process since the absence of the thiol compound eliminates the bad mercaptanlike odor, and the final product is a clear colorless solution that can be used as such as chelant and/or dispersant with no further treatments such as removal and recovery of the polymer.

Effect of Temperature (General)

Polymerization of acrylic acid in water is exothermic and it reaches temperatures as high as 100° C. We observed the largest chelation value for Ca²⁺ when the applied temperature was close to 100° C and is maintained during polymerization. An optimum temperature of ~ 95°C is preferred for this process since experiments with a pressurized reactor >100°C did not yield polymers with higher Ca²⁺ chelation. This may possibly be due to the rapid decomposition of the persulfate initiator at temperatures above



Figure 2 Contour plot. Interaction factor: Initiator × temperature effect on M_w . HACA = 215 g (21 wt %). Addition time = 1 h.

100°C.^{16,19} The decomposition of persulfate at above or below 100°C produces bisulfate (uncatalyzed); therefore, the resulting Poly-A solution is very acidic, pH \sim 1.95, regardless of the reaction conditions.

Critical examination of the polymerization reactions data reveals that the applied temperature is important, namely, whether the reaction is carried out isothermally or not. In general, temperature affects the molecular weight as discussed in the next section on statistical analysis. In the 80-100°C range, the molecular weight decreases rapidly, especially as the temperature nears 100°C (see Fig. 2). We also found that the most reproducible polymerization, resulting in highchelating Poly-A, occurred when the applied temperature was close to the exotherm temperature, about 95°C, and was kept as isothermal as possible (Fig. 3). Furthermore, we could not correlate average molecular weights to the MCV in this set of experiments. This observation suggests that isothermal polymerization at \sim 95°C induces structural features that have greater impact on the MCV than has molecular weight. This is consistent with nonisothermal free-radical polymerization which is a complex phenomenon because of the sudden changes of temperature. $^{10,11}\ {\rm The}$ abrupt changes of temperature induce a propagation of thermal waves that affect the rate of polymerization and the rate of initiation; consequently, these changes will affect the structure and molecular weight distribution of Poly-A.

Aqueous Gel Permeation Chromatography (AGPC)

Gel permeation chromatography²⁰ was performed to determine whether the average molecular



Figure 3 Solution temperature profile during polymerization. Acrylic acid concentration 22 wt %; initiator 0.003 wt %. **x** corresponds to an applied temperature = 70°C and allowing cooling of the solution (MCV = 522). Solid triangle is at 80°C with cooling (MCV = 527). Squares are at 80°C with minimal cooling (MCV = 600). Solid diamonds are at 96°C with minimal cooling (MCV = 630).

weights of Poly-A from near isothermal polymerization are related to high chelation for Ca^{2+} . There is indeed a direct relation between Ca^{2+} chelation and molecular weight. The higher the weight average molecular weight, the higher the maximum chelation value (Fig. 4). Figure 4 shows a moderate linear relation between M_w and the MCV ($R^2 = 0.7758$) with a large degree of scatter that is undoubtedly related to the difficulty of



Figure 4 Plot of M_w versus MCV. The error bars correspond to 13% RSD. (Relative Standard Deviation—defined as $\frac{\text{standard deviation}}{\text{mean}} \times 100.$)

obtaining the same M_w per run and to other requirements that may be needed for a large MCV, that is, structural contributions (see the sections on further characterization of Poly-A and modeling) from Poly-A. GPC characterization further gives the polydispersity of the samples. We did not observe a correlation between polydispersity and the MCV (see the next section on statistical analysis) but we found in our process that whenever the MCV was high the polydispersity value was \sim 4. The reproducibility of the synthesis of Poly-A was tested by keeping the following variables constant: applied temperature (95°C), ratio of glacial acrylic acid (212 g) to sodium persulfate (2.5 g), the rate of addition (in 60 min), and the duration of polymerization (2.0 h). Based on 12 runs using these conditions, Poly-A has a statistical average molecular weight (M_w) of 150,000 \pm 10,000 (see also the next section).

Statistical Analysis of the Poly-A Process

Free-radical polymerization has been studied extensively because of the ease of preparing polymers via this route; however, its fundamentals are complex as a consequence of the reactivity of the free radicals and the multiple factors that are involved in this kind of polymerization, that is, initiator, monomer, solvent, temperature, concentration of reactants, mixing, chain transfer, and percent conversion and whether the reactor is batch or continuous. In view of the complexity of the factors involved in the aqueous persulfate polymerization of acrylic acid, we carried out a design of experiments to define the best reaction conditions to obtain reproducibly Poly-A with a large MCV and to gain further insight into the Poly-A's high Ca^{2+} chelation capacity.

The process, for experimental-design purposes, is defined as the relation between the synthetic conditions and their effects on maximum chelation for Ca^{2+} and its dispersion. We decided to perform a factorial design since it allows one to study the combined effect of the factors on a response.²¹ It is a 2^{4-1} resolution IV factorial design. Resolution IV refers to a design in which no main factor is aliased with any other main factor or with any two-factor interaction, but two factor interactions are aliased with other. A total of 11 random experiments were performed to fulfill the selected 2⁴⁻¹ experimental design (eight runs with three center points). The eight runs correspond to the minimum requirement of 2k, where k represents the number of factors and in our case is

equal to 4.²¹ The three center points are to determine whether there is any curvature in the data.^{21,22} In our case, no curvature was observed and we repeated the center points to get an estimate of the error in our experiments.

The evaluated responses in the design are viscosity; MCV; molecular weights M_W (weight-average molecular weight), M_p (molecular weight based on the retention time of the chromatogram), and M_n (number-average molecular weight); polydispersity (PD), which is defined as $M_w/M_n \ge 1.1$, and dispersion (Dis). The bar graph shown in Figure 5 summarizes the results of the experimental design. The data pertaining to dispersion will be discussed in the last section of this article. Further, as M_w and dispersion are inversely related (r = -1, correlation coefficient) discussion will be limited to M_w only in this section (see also section on dispersion). Bars that are greater than zero indicate a positive relationship between factor and response, whereas bars less than zero show an inverse relationship between factor and response. The size of the bar expresses the strength of the relationship. From this graph, one can extract the factors that can affect MCV and dispersion.

Figure 5 is a complex array of factors and responses for Poly-A's synthetic process and it depicts, in a nutshell, the intricacies of acrylic acid free-radical polymerization. The factors are divided in two groups: main and interaction factors. The main factor refers to the primary variables of interest in the experiment and they are temperature, addition time, concentrations of monomer and initiator. Interaction factors refer to interdependence among factors, and they are present when the effect of a factor depends also on the level of one (or more) of another factor.^{21,22} We will represent, in general form, the interaction factor as A^*B , where A and B are two different main factors. Our experimental design can only look at the main factors and $\frac{1}{2}$ of the interactions. Resolution IV has aliases of the two-factor interactions; therefore, the six two-way interactions corresponding to the four factors²¹ collapses to three two-way interactions, which, in turn, are coupled with one another. Thus, the three aliases are

- Acrylic acid amount (HACA) \times initiator amount \Leftrightarrow addition time \times applied temperature.
- HACA × addition time ⇔ initiator amount × applied temperature.



Figure 5 Regression bar plot for the Poly-A experimental design. Regression coefficients for the responses are represented as bars. Bars > 0 indicate a positive relationship between a factor (i.e., concentration of acrylic acid, HACA, etc.) and the responses. Bars < 0 indicate an inverse relationship between the factor and a response. The larger the bar, the stronger the effect for each of the responses. (a) Significant at the P = 0.05 level. (b) Significant at the P = 0.1 level.

 HACA × applied temperature ⇔ initiator amount × addition time.

It is suffice to say that we cannot differentiate coupled interaction factors from each other based on our small design. This means that if one sees, for example, a statistically significant effect of HACA \times temperature on M_w , then, one cannot distinguish it from initiator \times addition time. However, almost always, the important interaction will have the significant main factors. Therefore, in this article, we analyzed, qualitatively, both two-factor interactions independently to determine their similarities and differences.

There is a large number of factor-response units presented in Figure 5; hence, we will attempt to explain qualitatively how they affect the MCV. Furthermore, the data in Figure 5 are not comprehensive, namely, there are factors and responses which are not included, for example, factors such as pH, percent conversion (we carried out the polymerization to high conversion), and tacticity. Tacticity as a response will be discussed in this article since polymer configuration can impart properties to the polymer that may or may not enhance the MCV.

The pH of polymerization is known to be important in aqueous free-radical polymerization. Anseth et al. found that the rate of polymerization increases, and they found that the rate is the highest at low pH, about 2.²³ Our polymerization was carried out in unbuffered solutions and the pH decreases as the reaction proceeds to a value of ~ 2.0 . We did not monitor the pH during reaction but one would expect that it would decrease quite rapidly since bisulfate is formed during the homolysis of persulfate. Hence, we can assume that our polymerization reactions, based on pH, occur quite fast.

Before we examine the bar graph on experimental design (Fig. 5) more closely, it is important to point out that all polymerization experiments were carried out at high percent conversion, indicating that the average molecular weights reported herein are cumulative average molecularweights. This kind of average molecular weight may or may not differ from the kinetic (instantaneous) average molecular weights depending on the reaction conditions.¹⁰ In general, the average molecular weight will depend on the ratio of monomer to initiator; therefore, in the case of high-conversion polymerization, we have two general situations²⁴: (a) Provided that the following conditions hold: monomer concentration decreases with conversion as it is used up, the initiation rate remains constant, propagation is irreversible, and termination is by either coupling or disproportionation, then the average molecular weight decreases and the average chain length decreases also with conversion. (b) If the rate of initiation decreases with conversion because the initiator is consumed, then the average molecular weight tends to increase.

Simple inspection of Figure 5 suggests clearly that the main factor—concentration of the initiator—is the variable that bears the greatest effect on the Poly-A process. It has a strong inverse relation to the average molecular weights, viscosity, and MCV and a direct effect on polydispersity (PD). The initiator effect is not unexpected since free-radical polymerization is intimately related to the concentration of the initiator. This is clearly seen in the mathematical relation for the kinetic (instantaneous) number-average degree of polymerization, $\bar{X}_n^{10,11}$:

$$\bar{X}_{n} = \xi \, \frac{k_{p}[M]}{(fk_{d}k_{t}[I])^{1/2}} = \frac{k_{p}^{2}[M]^{2}}{k_{t}R_{p}} \tag{2}$$

The termination mode affects X_n and the parameter ξ characterizes the proportion of chains that have undergone termination by recombination (coupling), and it takes the value interval $\frac{1}{2}$ $\leq \xi \leq 1$, where $\frac{1}{2}$ corresponds to the extreme where all termination is by disproportionation, and 1, when all termination is by coupling.¹⁰ If combination is the exclusive mode of termination, then, on average, the growing chain will double in length; on the other hand, if termination is by disproportionation exclusively, then there is no change in length in the process.¹¹ Equation (2)shows a very significant aspect of free-radical polymerization. \bar{X}_n is inversely proportional to the concentration of the initiator, that is, increase of the initiator results in short polymer chains; hence, the resulting polymer will have a low number-average molecular weight polymer at the low percent conversion region. The case of \bar{X}_w (kinetic weight-average degree of polymerizations) is less straightforward to visualize since it related to \bar{X}_n as follows:

$$\frac{\bar{X}_w}{\bar{X}_n} = 1 + p \tag{3}$$

where p stands for growth probability. The value of p becomes smaller as initiator concentration increases; therefore, \bar{X}_w also decreases with increase of the initiator concentration. This situation should prevail also at high percent conversion because a high persulfate concentration assures an initial low instantaneous average molecular weights and a constant initiation rate throughout the polymerization. The inverse relation of initiator (persulfate) concentration to the MCV seems to lead to a correlation between molecular weight and the MCV. This is a logical relation since the molecular weight of Poly-A determines the amount of carboxylates available for chelation per molecule.

Although the MCV is inversely related to the initiator, PD has a positive relation with the initiator concentration, that is, PD becomes larger upon increase of the initiator concentration even though M_w and M_n are both affected in the same fashion by the initiator. The reason for such a result lies in the behavior of the both average molecular weights at high percent conversion. The cumulative average molecular weights, M_w and M_n , decrease as the degree of conversion becomes larger as long as the rate of initiation rate remains constant during polymerization; however, their rates of decrease are different, where M_n decreases faster than does M_w when the degree of conversion exceeds 80%.¹⁰ Another way to look at this situation is that small molecules contribute to M_n the same as do large mol-ecules, whereas in the case of M_w , small mole-cules have less contribution^{10,23}; therefore, as the initiator concentration increases, more small molecules are formed, which makes M_n smaller than M_w . The consequence is a larger gap between M_w and M_n , namely, PD becomes larger.

Our experimental design shows that an increase in *monomer concentration* (HACA), at 95°C and a fixed concentration of persulfate, affects the average molecular weights differently (see Fig. 5). The response is mildly positive for M_w and M_p but moderately inverse for M_n . HACA has a strong

positive relation to PD and a moderate positive relation to the MCV and viscosity. Before discussing the results from the HACA studies, we will review some relevant information from the literature of acrylic acid polymerization kinetics that will help to explain the effects of monomer concentration (HACA).

Henton et al.²⁵ reported recently that the rate of decomposition of persulfate speeds up in the presence of acrylic acid $(k_d \text{ increases})$, and this becomes more significant at pH \sim 2. Further, decomposition is faster when the acrylic acid concentration is low. A consequence of this initiatormonomer interaction is that the rate of polymerization, R_p , will show a $\frac{3}{2}$ power dependence on the monomer concentration, acrylic acid.¹¹ This ³⁄₂ dependence was also observed by others.^{13,14,26} Scott and Peppas²⁶ showed the unusual ³/₂ dependence on monomer concentration at both acid and basic regimes, whereas the initiator dependence remains ¹/₂ during their studies on the kinetics of aqueous persulfate polymerization of acrylic acid. Ishige and Hamielec²⁷ and Riggs and Rodriguez²⁸ reported also a 3/2 dependence on monomer concentration for the case of aqueous persulfate polymerization of acrylamide.

Cutie et al.¹² also found that M_n decreases at a high percent conversion and this result implies that the kinetic constants, especially, k_d for initiation, are independent of conversion. Scott and Peppas²⁶ demonstrated such independence by plotting $\ln(R_p)$ versus $\ln(1-p)$ at pH ~ 2 and obtained a straight line. The variable (1-p) refers to the probability of chain termination. They selected the data away from nonisothermality to avoid variations of the kinetic constants due to temperature.

Our experimental conditions, for the effect of monomer concentration, call for an addition time of 60 min, applied temperature \sim 95°C, and fixed initiator (persulfate) concentration, $\sim 0.01M$. The pH of our reaction is ~ 2 as indicated earlier in this article. Based on the result that the kinetic constants are independent of conversion at pH $\sim 2,^{26}\,M_n$ should decrease at high conversion just as reported elsewhere. 12,27,28 At each HACA increase, the polymerization results in a Poly-A whose cumulative number average molecular weight is smaller than that originated from a lower concentration. On the other hand, M_{w} increases when HACA increases; consequently, one would expect larger PDs with increases of HACA. just as our results concluded (see Fig. 5). One can explain these results in terms of the kinetic chain

length. This term is defined as the average number of monomer molecules polymerized per each radical that initiates a polymer chain, or, alternatively, it is the average number of steps of growth per effective radical.^{10,11,28} The kinetic chain length depends of the ratio [monomer]/[initiator]^{1/2}; therefore, as HACA increases and the persulfate concentration is kept constant, we favor the formation of large-sized molecules. As explained earlier, large-size molecules will contribute more to M_w than to M_n .

HACA has a moderate positive effect on viscosity. This is not unexpected because, in most cases, when M_w increases, so does viscosity. This occurs because the viscosity-average molecular weight (M_v) lies closer to M_w than to M_n ; in fact, in special conditions, M_v and M_w are the same.²⁹

The opposite effects of *initiator concentration* and the monomer concentration on the MCV response means that for a large MCV value the resulting Poly-A should have a large weight-average molecular weight, M_w , rather than a large number-average molecular weight, M_n . Figure 4 shows a moderate linear relation between M_{w} and the MCV ($R^2 = 0.7758$) and there is a large degree of scatter in the data which is undoubtedly related to the difficulty of obtaining the same $M_{\mu\nu}$ per run and to other requirements that may be needed for a large MCV, that is, structural contributions from Poly-A. The relations of M_p and M_n versus MCV provide even weaker linear regression relations whose R^{2} 's are 0.5296 and 0.2718, respectively. Figure 5 shows that the relation between HACA and MCV is a positive one but mild in strength. Hence, the issue of a large M_w is important but not critical since addition time, the main effect that favors MCV the most, inversely affects M_{w} . This supports the idea that there must be other polymer structural contributions (see next section) in addition to molecular weight to determine the factors that controls MCV.

There should be also a correlation between viscosity and MCV since both are positive responses with respect to HACA, and there is a linear correlation between M_w and viscosity. However, our results show that both responses are not well correlated. Linear regression analysis, of the viscosity versus MCV data, gave a squared correlation coefficient, $R^2 = 0.067$. This unexpected result may be due to the fact that the viscosity was obtained at pH ~ 2 and the Ca²⁺ chelation values were obtained at pH ~ 9. We did not at-



Figure 6 Contour plot. Interaction factor: HACA \times initiator effect on MCV. Applied temperature = 90°C. Addition time = 1 h.

tempt to pursue the correlation at the appropriate pH.

Addition Time

The time in which the monomer and initiator are delivered to the reactor has a strong positive influence on the MCV, a mild positive relation to PD, and an inverse relation to the rest of the responses. This single variable brings into light the fact that the average molecular weights decrease as addition time increases, yet the MCV becomes larger at long addition. As already mentioned, there are other factors than molecular weights that come to play in the mechanism of chelation and in the improvement of the MCV. The average molecular weights tend to decrease with long addition times because we are lowering the ratio of monomer/initiator as addition time increases; therefore, the kinetic chain length theory predicts small-sized molecules. We could not determine an exact threshold average molecular weight in which Poly-A shows poor chelating properties; however, we did find that as long as the addition time is >1 h and temperature is between 80 and 95°C during polymerization, the resulting Poly-A will have excellent MCVs that are moderately related to molecular weights.

Temperature (Refers to Applied Temperature)

In general, the effect of temperature in free-radical polymerization is to increase R_p .^{11,12,30} Therefore, the results should be similar to that discussed above for an initiator. Figure 5 shows that, indeed, the temperature is inversely related to the MCV, PD, and viscosity and to all three molecular weights. The difference is on the PD where the initiator has a positive effect.

PD has an inverse relation to temperature but one should be cautious about this result because this relation occurs only when the concentration of acrylic acid is about 25 wt %. At 20 wt %, PD hardly changes when the applied temperature is increased. M_w is favored at high monomer concentrations and at fixed temperature, but as the temperature is increased, M_w decreases. Conversely, M_n is moderately unfavored at high HACA but its mild inverse relation to temperature warrants that M_n remains fairly constant with increase of temperature; therefore, the result is that PD decreases. In the low end of acrylic acid concentration, M_n is favored over M_w (smallsize molecules); furthermore, the temperature effect is minimized due to its similar strength on M_w and M_n ; therefore, for all practical purposes, PD will be low and will remain relatively constant as temperature is increased.

HACA × Initiator Amount ⇔ Addition Time × Applied Temperature

The significant main response for the discussion of these interactions is the MCV. Let us take, for example, the interaction factor HACA \times initiator and its effect on the MCV. Figure 6 shows that there is noticeable increase in the MCV as the initiator concentration decreases at a fixed HACA concentration, whereas the opposite does not show a great effect just as we saw for the case of HACA itself in Figure 5. Figure 7 relates these interaction variables to PD. Notice that in contrast to Figure 6 where the best region for the MCV is at high HACA, low initiator and low HACA correspond to a PD \sim 4. This means large



Figure 7 Contour plot. Interaction factor: HACA \times initiator effect on PD. Applied temperature = 90°C. Addition time = 1 h.



Figure 8 Contour plot. Interaction factor: temperature \times initiator effect on MCV. HACA = 215 g (21 wt %). Addition time = 1 h.

 M_w but small M_n . This emphasizes, once again, the positive effect of M_w on MCV. The inverse relation of HACA \times initiator, seen in Figure 5, with respect to MCV comes from the fact that increase of both factors lead to low average molecular weights and large polydispersity due to an increase in R_p . Note that large PD does not necessarily mean large MCV; in fact, we did not find any statistical correlation between PD and MCV. However, we found, in our process, that a Poly-A with a PD \sim 4 most likely will have a large MCV.

Similarly for the interaction – addition time \times temperature-addition time controls the concentration of acrylic acid and initiator per unit of time and temperature has similar effect on the system as the initiator. Therefore, long addition times at high temperatures led to Poly-As with low M_w 's and low MCVs. The optimal region is addition time about 1 h and temperature between 80 and 95°C.

HACA × Addition Time ⇔ Initiator × Temperature

These two-factor aliases have a fairly strong inverse relation with MCV. Figure 8 shows the influence of initiator and temperature on MCV. The key point is that at high persulfate concentration and high temperature the resulting Poly-A possesses low MCV and low average molecular weights. The optimum conditions are low initiator and temperature between 80 and 95°C. Higher temperatures than 95°C leads to Poly-A with low MCV even if the persulfate amount is at the optimum amount (3–4 g). This decline of MCV, for Poly-A's prepared at temperatures higher than 95°C, is attributed to a decrease in M_w due to



Figure 9 Contour plot. Interaction factor: temperature \times initiator effect on polydispersity. HACA = 215 g (21 wt %). Addition time = 1 h.

possible decomposition of persulfate at higher temperature and increased R_p (see Fig. 8), although structural factors may be involved as well. Figure 9 shows the trend of PD; once again, the region corresponding to the best MCV is the region where Poly-A has a PD ~ 4 as we have stated above. This reinforces more the idea of M_w being the critical average weight for a high MCV.

The HACA \times addition time effects on MCV, M_n , M_w , and PD are shown in Figures 10–13. Most of these contour plots show complex relations. In the case of MCV, the main trend is that it becomes larger at a slow addition rate of acrylic acid and the initiator. However, at a longer addition time, increase in HACA decreases the MCV. The faster the addition, the lower MCV of the resulting Poly-A. Figure 11 exposes the complex contour plot for M_n and the striking result is that M_n is generally favored at a short addition time,



Figure 10 Contour plot. Interaction factor: HACA \times addition time effect on MCV. Initiator = 4 g. Applied temperature = 90°C.



Figure 11 Contour plot. Interaction factor: HACA \times addition time effect on M_n . Initiator = 4 g. Applied temperature = 90°C.

whereas M_w decreases at fast rate of addition and low concentration of acrylic acid (Fig. 12). Figure 11 shows also a reversal of the M_n trend at addition times longer than 1 h and at high acrylic acid concentrations. This is precisely the effect of interaction. When we relate these observations to Figure 10, it is clear that the concentration of acrylic acid must be less or equal to 21 wt % (~ 215 grams of acrylic acid), and an addition time >0.9 h to obtain a high chelating Poly-A with PD ~ 4.

HACA × Temperature ⇔ Initiator × Addition Time

These interactions affect weakly the MCV, and we will not expand much on this interaction except that these interactions reiterate that for best results the initiator and HACA must be delivered



Figure 12 Contour plot. Interaction factor: HACA × addition time effect on M_w . Initiator = 4 g. Applied temperature = 90°C.



Figure 13 Contour plot. Interaction factor: HACA \times addition time effect on PD. Amount of initiator = 4 g. Applied temperature = 90°C.

at a slow rate and the temperatures should not exceed 95°C.

Further Characterization of Poly-A

In our experimental-design studies, we concluded that the MCV is related to molecular weight and structural features of Poly-A. To investigate the latter, Poly-A was characterized by viscosity, FTIR, NMR, and Raman techniques. The *viscosity* of the Poly-A solutions was measured with a Brookfield viscometer. Figure 14 shows the classical polyelectrolyte behavior of viscosity versus pH in which the viscosity increases with increase of pH due to extension of the polyelectrolyte coil. The increase slows down at high pH (plateau) and



Figure 14 Plot of pH versus Brookfield viscosity. Poly-A prepared with the following conditions: addition time, 60 min; applied temperature, 95°C; and 21 wt % glacial acrylic acid (HACA).



Figure 15 FTIR spectrum of Poly-A. Region from 1500 to 699 cm⁻¹.

there is an eventual decrease of viscosity when the amount of base is in large excess. The plateau and the reversal of viscosity is due to the counterion (Na⁺) from the base which screens the charge of the polyelectrolyte; therefore, there is a decrease of the electrical field responsible for the expansion of the polyelectrolyte chain. As this field decreases, the polyelectrolyte recoils and the viscosity decreases again.³¹

FTIR was used also to characterize our Poly-A. Bisulfate, a by-product from persulfate decomposition, was removed from Poly-A by dialysis against water. The amount of bisulfate was determined on the basis of sulfur (amount of sulfur after dialysis = 45 ppm). Water was then removed from the dialysis-treated Poly-A solution using a rotatory evaporator at <80°C under a vacuum, and FTIR was then recorded for the solid (Fig. 15). The FTIR spectrum of our Poly-A exposes some degree of syndiotacticity in conjunction with some isotacticity. This conclusion arises by comparison with spectra from Monjol and Champetier,³² wherein the region of 1500-700 cm^{-1} is important for such a determination. However, the FTIR results are different from those obtained using NMR. ¹H- and ¹³C-NMR spectra of several samples of our Poly-A show them to be atactic regardless of its MCV, and no signs of stereoregularity were detected. We confirmed the tacticity in two ways: by comparing our spectra to the reported NMR spectra of a known atactic sample,³³ and by obtaining NMR spectra of an atactic Poly-A from a vendor. The differences between the FTIR and NMR results cannot be reconciled at this time.

The results from the NMR analysis agree with the work of Laborie^{34,35} and Chapiro and Dulieu.³⁶ They found that their gamma ray-initiated aqueous polymerization of acrylic acid resulted in an atactic polymer, especially whenever the concentration of the monomer was less than 25 wt %. Our procedure (see Experimental section) utilizes a monomer concentration in the range of 20-25%by weight. Moreover, a steady slow addition of the monomer, during polymerization, ensures a low concentration of the monomer per unit of time during polymerization. The difference in initiation should not influence the tacticity of the polymer; hence, one would expect our Poly-A to be mostly atactic. The atactic Poly-A with a molecu-



Figure 16 FT–Raman spectra of (1) Poly-A and (2) dried Poly-A.

lar weight ~ 3000 daltons, used as a standard in the NMR analysis, provided an average MCV of 417 mg of CaCO₃/g of Poly-A. This is still lower than that obtained with the sample of ours but its M_w is far smaller than those tested in this study.

There is a requisite of an applied temperature greater than 80°C but less than 95°C in order to obtain an atactic Poly-A by our process. In support to our results, Chapiro and coworkers^{36,37} postulated that carboxylic monomers containing a vinyl group form organized structures (oligomeric) with themselves via hydrogen bonding. These monomer associations are claimed to account for the formation of stereoregular Poly-A and they disrupt and revert to a monomer–solvent complex when the solvent is polar and the temperature is high, and the resulting Poly-A is atactic. Furthermore, water—due to its polarity and strong hydrogen-bonding capability—should favor the disruption of such an association; it has been reported that atactic Poly-A readily forms in water, especially at a concentration below 25 wt % of acrylic acid.^{34–37}

Raman analysis of a 20% solution of Poly-A, with very good chelation (MCV = 756 mg of $CaCO_{3}/g$ of Poly-A), indicates that the polymer exists predominantly in one form based on the C=O region of the spectrum (Fig. 16). However, a similar experiment on a solid sample (isolated after drying) of the same Poly-A shows that a significant portion of the carboxylic acid groups exists as a hydrogen-bonded dimer. This scenario is consistent with the Raman spectroscopic work of Kitano and coworkers.³⁸ Tanaka et al. showed the presence of dimer, resolved the dimer from monomer in solution, and suggested that a "cooperative" H-bonding may form in a Poly-A aqueous solution that may explain the observed behavior in the Raman spectra.³⁹ In contrast to our Raman results, NMR analysis shows no difference between the spectra of solid and liquid samples of Polv-A.

Figure 17 illustrates a set of surprising results wherein the chelation values for calcium, after dissolving the dry sample of Poly-A in water, are lower than those observed in the original sample



Figure 17 Chelation value plots. Circles correspond to the original sample of Poly-A ($M_w = 192,700$) before drying. Squares are for the dried Poly-A (overnight drying at 72°C). Triangles represent the case after heating overnight the dry Poly-A sample in distilled water at 60°C.

prepared in water. The chelation values can be improved to some extent by heating the dry sample in water at 60°C overnight. However, they do not return to their original values. Several scenarios may provide an insight into this issue. Hydrogen-bonded dimerization of some of the carboxylic acid groups of Poly-A during the drying process makes them unavailable for chelation to calcium. Addition of water followed by heating up to 60°C helps to break the H-bonded dimers to produce more free carboxylic acid groups and thus improve chelation, although it does not yield the original chelation values. The disruption of these H bonds can also be related to the hydration of the polymer chains.^{40,41} This dramatic decrease of MCV upon drying is in favor of keeping the Poly-A in solution when used as a chelant.

For water-soluble polymers, water is the crucial factor that governs the structures and properties of polymers in aqueous solution. At the same time, the properties of water reflect the changes in the structures and properties of the polymers. The water in polymer solutions consists of "bulk" water, "hydration" water around polymer molecules, and "interstitial" water in compartmentalized spaces surrounded by the polymer network.^{40,41} It is possible that rehydration of dried Poly-A does not yield into the original polymer network present before removal of water from the Poly-A solution. Another possibility is that during the drying process an intracyclization (anhydride formation) reaction occurred, and it reduced the number of available carboxylic groups for chelation.^{42,43}

Chelation of Poly-A versus Commercial Polyacrylics: Effect of pH and Molecular Modeling

As discussed before and in the Experimental section, maximum chelation occurs at a very low concentration of Poly-A. The maximum chelation value or MCV was used to analyze two important issues: (i) comparison of MCVs between our Poly-A and commercial Poly-A's and (ii) and the reproducibility of the MCV from Poly-As synthesized under the same conditions. To answer the latter issue first, we analyzed a set of 12 runs—with an average M_w 150,000 \pm 10,000—that yielded an MCV of 680 \pm 104 mg CaCO₃/g Poly-A. The standard deviation value represents 15% RSD (as defined in Figure 4), and as stated earlier in this article, the relationship of M_{m} and MCV bears a large degree of scatter. In contrast to our Poly-A, a set of seven commercial Poly-A's, whose molecular weights (M_w) ranged from 60,000 to 250,000 (126,000 ± 69,320), provided an average MCV of 566 ± 55 mg CaCO₃/g Poly-A. Our other set consisting also of seven different Poly-As, synthesized in our laboratory, with a range of molecular weight (M_w) of 67,000–256,000 (126,429 ± 68,685), yielded an average MCV of 662 ± 40. Thus, it is clear that our Poly-A has a greater chelating capacity than that of commercial polyacrylics tested in our laboratory.

The chelation of calcium ions by Poly-A in aqueous solution is complex in contrast to chelants like EDTA. While the chelation of Ca²⁺ EDTA forms five-coordinate complexes bv through nitrogen and carboxylate anions, it is believed for Poly-A to involve classical chelation as well as a polyelectrolyte effect.⁴⁴ The latter effect explains the unusually high chelation ratio when compared to the theoretical ratio of 0.5.44 The polyelectrolyte effect refers to the behavior of a polyelectrolyte at very dilute solutions in which the polymer chain expands due to the electrostatic repulsion of the charges from its ionization. Ionization is greatly favored at pH 9.5 since the pK_a for Poly-A is about 4.8.³¹ The carboxylate anions are more available to bind Ca²⁺ under these conditions. At a low concentration of Poly-A and at pH \sim 9.2, the Ca²⁺ may be bound to both a carboxylate anion and a hydroxide ion. As the concentration of Poly-A increases, there is competition between polymer chains for the reduced amount of Ca^{2+} present in the solution; therefore, the number of calcium ions per gram of chelate decreases. The hydroxide anion is replaced by Poly-A as its concentration increases during titration.

The change of pH has a profound effect on the chelating capacity of Poly-A as shown in Figure 18. More significantly, at pH > 7.3, Poly-A becomes a better chelant than EDTA. Furthermore, the leveling off takes place faster with EDTA than with Poly-A. We used the values for 80% chelation, simply because Poly-A and EDTA have different chelation values versus percent chelation plots.⁴ In other words, we chose the 80% chelation level solely for comparative purposes. It is noteworthy to point out that a comparison of Figures 14 and 18 shows that the chelation value of Poly-A and viscosity begin to plateau at about the same pH; therefore, one can speculate that this plateau may not be attributed only to a lack of free carboxylate but also to a lack of expansion of the polyelectrolyte as the pH for chelation increases. Coil expansion ceases when a critical amount of



Figure 18 Calcium chelation versus pH for (1) Poly-A and (2) EDTA. The chelation values for Poly-A and EDTA are at 80% chelation.

counterions (Na⁺ from the base) screen the charges of the ionized carboxylate, and further addition of the base leads to recoil of the polyelectrolyte chain that not only hinders available free carboxylates, but also prevents the diffusion of the doubly charged calcium into the coiled chain to reach the carboxylates. Indeed, we observed that a commercial polyacrylate containing a high percent of Na⁺ had a minimal Ca²⁺ chelation capacity.

One might wonder why our Poly-A has specific structural qualities that allow large MCVs. Molecular weight seems to be one factor but the scatter on the MCV versus molecular weight points to the possibility that other factors may be involved in the improvement of the chelation capacity of Poly-A. Those factors may be related to the structure of Poly-A, that is, tacticity and defects in the polymer chain due to head-to-tail inversion. Spectroscopic techniques were not straightforward to evaluate these structural factors. Therefore, we decided to utilize *molecular modeling on Poly-A* to gain further understanding of how the structure and tacticity of Poly-A are related to chelation.

The modeling studies on chelation by Poly-A were carried out with an eight-unit oligomer of acrylic acid. No solvent was considered in this calculation. The molecular modeling studies suggest that the higher chelation values are related to the degree of tacticity and the head-to-tail inversion. This is supported by the results from an eight-unit atactic oligomer in which a single cation may be associated with two to four acid units. On the other hand, for the case of an isotactic or syndiotactic octamer, a single cation can form complexes with five to six acid units. These results clearly suggest that the atactic polymer should have more chelating capacity per polymer chain than that of a stereoregular one. This, of course, leads to higher MCVs.

The head-to-tail inversion analysis revealed an optimum concentration of head-to-head/tail-totail defects that will maximize ion binding. Chelation was modeled using three different atactic 16-unit oligomers: The first chain contained no defects, that is, every polymer unit was connected in a head-to-tail fashion. The second modeling was done with two defects that is, two monomers were flipped to have two head-to-head and tail-totail connections along the polymer backbone. Finally, the third chain contained four head-tohead/tail-to-tail defects. The strongest binding was observed in the simulations containing two defects per oligomer. Thus, it is possible that our Poly-A, in addition to being mostly atactic, has the correct amount of defects in contrast to the commercial polyacrylics.

We noticed from our work that two Poly-As of similar weight-average molecular weight will have different MCVs if one was prepared at conditions of temperature $>95^{\circ}$ C, and the other was prepared by using a long addition time but a temperature <95°C. The one prepared at <95°C and a long addition time will have a larger MCV than that of the other. It has been reported that the effect of increasing the polymerization temperature is an increase in the extent of head-tohead placement, but the effect is small (ca. 1–14%) depending on the monomer.¹¹ It is quite possible that in our situation we are inducing more defects to the Poly-A as we increase the temperature; therefore, we depart from the optimum number of defects calculated from the molecular modeling. An increased number of headto-head placements in the polymer chain will cause the carboxylates to be in close proximity and this will induce steric strain on the polymer coil that will make difficult the accommodation of the Ca²⁺ for chelation. It is believed that Poly-A makes an 8-membered ring with divalent cations.⁴⁵ A larger number of these head-head defects will not allow this large chelate ring that, in principle, is rare due to steric strain; however, they should be possible with Poly-A due to its large number of carboxylates and the flexibility of the chain.

Molecular modeling studies suggest that a single cation binds two to four acid groups in atactic polymer. If we assume that two carboxyl groups (two acrylic monomer units, $M_W = 144$) are needed to chelate one calcium ion (40), then the theoretical MCV should be $40 \times 100/40 \times 1000/$ 144 = 694. Based on our average MCV of 680 mg CaCO₃/g Poly-A, each calcium ion requires an average of $2 \times 694/680 = 2.04$ carboxyl groups. In contrast, commercial polyacrylics would require a number of carboxyls >2.04 per calcium ion. Further support to the idea of having a mostly atactic Poly-A comes from the studies of Monjol who found that atactic acrylic polymers are favored during free-radical polymerization at high temperature.⁴⁶

In addition to the above studies, the relative binding affinities for Mg^{2+} , Ca^{2+} , Cu^{+1} , Cu^{2+} , and Fe^{2+} were also considered. The strongest interaction with Poly-A is observed with Mg^{2+} , followed by Ca^{2+} , Cu^{2+} , then Fe^{2+} . The weakest binding corresponded to Cu^{+1} . Hence, it may be possible to use Poly-A for selective ion separations.

Dispersion Results

Although chelation was the main objective of this project to compete with EDTA and DTPA, we soon realized that an important aspect of Poly-A with different molecular weights may be their efficacy in dispersing Ca²⁺ and Fe³⁺ ions. We first discuss the results on dispersion of CaCO₃. The statistical analysis shows that the effect of initiator and temperature were the most important factors that control the dispersing properties of the resulting Poly-A (M_w and dispersion are inversely related; r = -1, correlation coefficient; not shown in Fig. 5). Dispersion increased as the concentration of the initiator or temperature increased since such a condition favors lower molecular weight polymers (Fig. 19). Addition time also has a direct relation with dispersion since longer addition time generates low molecular weight Poly-A. The requirement of having low molecular weight Poly-A is in accord with the phenomenon of CaCO₃ dispersion.⁴⁷ Essentially, dispersion consists of adsorption of the polyelectrolyte on the positively charged edges of the mineral particles and prevents the association of the particles. For this to happen, an important requirement is that the polyelectrolyte must have a high anionic charge density to guarantee strong electrostatic interaction with the crystal surface of the mineral.⁴⁸ The reason that low molecular weight Poly-A has better dispersing properties is related to the chain length of the Poly-A. Low molecular weight polyelectrolytes extend more easily as they becomes ionized, thus exposing a greater number of carboxylates.^{47,49} Another advantage of low molecular weight Poly-A is that its molecular weight distribution contains contributions from the very low end of the distribution that helps intercalation into the swollen and the poorly sterically accessible interfacial layers of the mineral particle. This process also prevents association of particles and thus prevents precipitation in solution.⁵⁰

Our dispersion values are similar to those obtained with commercial Poly-A's, in spite of the fact that our Poly-A—used for this purpose—has a somewhat larger molecular weight than that of the commercial ones. In the case of the dispersion of Fe^{3+} , we find that our Poly-A fared slightly better than did some of the commercially available Poly-A's. As in the case of the calcium ion, the lower molecular weight polymer has better dispersing properties.



Figure 19 Effect of applied temperature (°C) and initiator amount on dispersion of $CaCO_3$. Polymer prepared with an addition time of 60 min and monomer (HACA) concentration of 21 wt %.

CONCLUSIONS

We synthesized high Ca²⁺ chelating Poly-A by persulfate-initiated polymerization of acrylic acid in water. An experimental design was used to optimize the process. The critical variables are the amount of initiator, addition time of the monomer and initiator, and constant applied temperature. Near-isothermal polymerizations, with temperatures greater than 80°C but less than 100°C, produce a high chelating polymer. At temperatures greater than 100°C, the resulting polymer shows lower chelation values, presumably due to rapid decomposition of persulfate and possible increase of head-to-head defects in the chain based on molecular modeling. The elimination of the octanethiol as a chain-transfer agent eliminates the odor and color problem observed previously. It also improves the range of the molecular weight of the polymer. The MCV has a moderate correlation with the weight-average molecular weight but a weak correlation to the numberaverage molecular weight. The moderate correlations of MCV with the average molecular weights indicate possible contributions from the polymer structure. NMR, FTIR, and molecular modeling studies shed some light on the possible relation between the structure of the polymer and its high MCV. According to the NMR and molecular modeling studies, our Poly-A is atactic, although FTIR data show some degree of syndio- and isotacticity.

Atactic Poly-A must be favored in our optimum conditions because high polymerization temperature (80–95°C) and longer addition time (steady low concentration during reaction) promote atacticity, and a small amount of initiator favors moderately high molecular weight. It is possible that the commercially available Poly-A's do not possess the same structural attributes. Hence, they do not provide as high an MCV as do our Poly-A's. The dispersion properties are dominated by conditions that promote low molecular weight, and our resulting Poly-A's fare very well against commercially available dispersing Poly-A's.

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