The Role of pH, Ionic Strength and Monomer Concentration on the Terpolymerization of 2-Acrylamido-2-methylpropane Sulfonic Acid, Acrylamide and Acrylic Acid

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ABSTRACT

The current study examines the effects of important factors (namely, pH, ionic strength and monomer concentration) on the terpolymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamide (AAm) and acrylic acid (AAc). A good understanding of how these factor levels affect terpolymerization reactivity ratios, and terpolymer composition, microstructure and molecular weight paves the way for the synthesis of custom-made polymers for specific applications. For the range of conditions studied, ionic strength has the greatest influence on reactivity ratios; results indicate that cross-over behavior exists for AMPS-based reactivity ratios. No clear correlation is observed between pH and reactivity ratio estimates (for $5 \leq pH \leq 9$), but parameter estimation results suggest that the incorporation of acidic comonomers (AMPS and

AAc) is affected by pH within this range. Finally, monomer concentration has a dominant impact on molecular weight averages, even when other factors are varied.

1. INTRODUCTION

The aqueous phase terpolymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamide (AAm) and acrylic acid (AAc) is an interesting and largely unstudied system. This new terpolymer has only recently appeared in the literature, with applications ranging from enhanced oil recovery [1] to controlled drug delivery [2]. Typically, existing studies focus on the final properties of the material (swelling behavior, thermal and mechanical stability, etc.) [1,3,4], but investigating the terpolymerization kinetics is equally important [5]. The bulk polymer properties (and, by extension, properties relevant to the final application) depend on the terpolymer microstructure, therefore a clear understanding of the terpolymerization kinetics is invaluable.

The kinetics of an associated copolymer, acrylamide/acrylic acid, have been well-studied. Riahinezhad et al. [6], among others, have shown that experimental conditions (that is, the pre-polymerization solution properties) can significantly impact polymerization kinetics and the resulting copolymer. Since the AAm/AAc copolymer is a polyelectrolyte, pH, ionic strength and monomer concentration are all influential variables during synthesis [7-10]. AMPS also exhibits polyelectrolyte behavior, so one might expect that solution properties will also affect AMPS/AAm/AAc terpolymerization.

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In looking at extensions from the AAm/AAc copolymer to the AMPS/AAm/AAc terpolymer, it is important to note that binary observations do not always apply to the ternary system [11]. In the past, many researchers have used copolymerization results to predict terpolymerization behavior. Although this may work for some cases, it is an approximation, as it effectively ignores the presence of the third comonomer. A third comonomer will inevitably change the reaction conditions and, by extension, the polymerization kinetics. Therefore, although we can look to the AAm/AAc system for guidance, new terpolymer-specific investigations are needed.

The current study examines the effects of solution properties on the terpolymerization of AMPS/AAm/AAc. Specifically, optimally designed experiments (using the error-in-variables model (EVM) design) [12] and a definitive screening design allow us to select pre-polymerization recipes with high information content so that we can learn about the entire system in just a few experimental runs. The experimental data are then used to estimate ternary reactivity ratios, which provide valuable information about the resulting terpolymer properties. A good understanding of how the solution properties affect terpolymer reactivity ratios, composition, microstructure and molecular weight paves the way for the synthesis of custom-made polymers for specific applications. In the current study, we are considering the terpolymer requirements for enhanced oil recovery, but the same principles can be extended to other applications.

1.1 Recipe Factor Effects

1.1.1 Effect of pH

The terpolymer of AMPS/AAm/AAc is a polyelectrolyte. That is, the macromolecule can contain covalently bound anionic or cationic groups (as a result of dissociation), which ultimately results in a charged polymer. These charges are extremely influential in terms of polymerization kinetics and should therefore be understood for customization purposes.

The comonomers AMPS and AAc are both acidic in nature, which means that dissociation (loss of the H^+ ion from the carboxylic or sulfonic acid group) occurs as pH increases. The amount of dissociation that occurs is often reported as the degree of ionization, α, and can be calculated according to Equation (1).

$$\alpha = \frac{10^{pH-pKa}}{10^{pH-pKa} + 1} \tag{1}$$

where pK_a is the acid dissociation constant, which varies by compound. Atta et al. [13] have reported that AMPS and AAc have pKa values of 2.3 and 4.2, respectively.

The rate of polymerization is a strong function of the degree of ionization. As the monomers (and resulting polymer chains) dissociate, they will contain like charges. These charges repel one another, which causes two significant changes in the system. First, the chain is forced to stretch out to separate the charges as much as possible (which eliminates the typical coil conformation of polymer chains). Second, the monomers and the radical chain contain like charges, which decreases the reactivity ratio of said monomers.

The effect of pH on the homopolymerization of AAm and the homopolymerization of AAc have been studied extensively, as have the copolymerization kinetics of AAm/AAc (see, for example, these references [14-17], [18-21],[8, 22-24]). To the best of our knowledge, a limited number of homopolymerization studies have been performed for AMPS [25]; it is more frequently used as a comonomer with AAm or AAc (see, for example, [26-31]).

A brief overview of pH effects is presented herein, as this research can help inform the current study. However, it is important to recognize that binary reactivity ratios (and, in general, copolymerization behavior) do not necessarily extend to terpolymer system [11]. So, by extension, the homopolymerization kinetics reported in literature may not always align with what we observe in terpolymer systems.

A recent study by Beuermann et al. [25] investigated the homopolymerization kinetics for the solution polymerization of AMPS using near-infrared spectroscopy and pulsed laser polymerization. The study included pH effects, as $\langle k_t \rangle / k_p$ values were compared over conversion for both the acid (AMPS) and salt (NaAMPS) forms of the monomer (where $\langle k_t \rangle$ is a mean termination rate coefficient and k_p is the propagation rate constant). Kinetic behavior was similar for both the acid form (where pH was very low) and the salt form (where pH = 7), suggesting that pH had no significant effect [25].
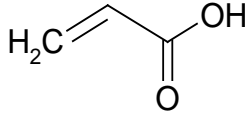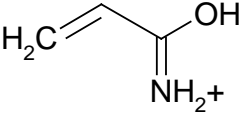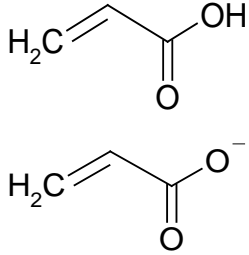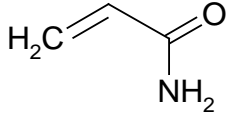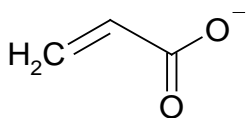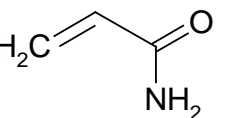
The effect of pH on the homopolymerization of poly(acrylamide) has been widely studied for many years (see, for example, [14-17]). The majority of these reports suggest that pH has little

effect on acrylamide homopolymerization kinetics, at least over the ranges studied. Some exceptions are an increase in k_p at pH 1 (compared to higher pH levels) reported by Currie et al. [14] and an increased rate of polymerization between pH 6 and pH 7 ([32] as reported by [15]). However, in general, other solution effects and reaction conditions are more influential than the solution pH.

Many poly(acrylic acid) kinetic studies (including these references [18-21]) have experimentally confirmed that the rate of polymerization of acrylic acid is significantly affected by pH; as the solution is neutralized (that is, as pH increases to approximately pH 7 and the degree of ionization, α, increases to 1), repulsion occurs between monomers and around the propagating chain, thus reducing the rate of polymerization for poly(acrylic acid). As the pH is increased beyond pH 7, an increased rate of polymerization is observed, likely due to charge screening effects [18, 21].

The general pH effects on the AAm/AAc copolymerization have also been well studied [22-24] and are summarized in Table 1. Copolymerization behavior at pH 2 (that is, where the acrylamide radical is protonated) has been studied by Cabaness et al. [22] and Paril et al. [23]; although pH effects are minimal in acrylamide homopolymerization studies, both copolymerization studies showed a reduction in AAm incorporation (and, subsequently, increased AAc incorporation) at low pH. Riahinezhad et al. [8] recently confirmed pH effects for the range of pH 3 to pH 7; experimental observations showed that the charged (AAc) monomer (at higher pH values) has lower additivity (that is, a lower reactivity ratio) due to charge repulsion.

TABLE 1: Effect of pH on AAm/AAc Polymerization Kinetics

pH	Monomer Forms Present		Effect on Reactivity Ratios $(r_i$ or $r_j)$
	Acrylic Acid (AAc)	**Acrylamide (AAm)**	
pH < 2	H_2C — OH, =O (carboxylic acid)	H_2C — OH, NH_2+	Increased r_{AAc}, decreased r_{AAm}
2 < pH < 6	H_2C — OH, =O (carboxylic acid); H_2C — O^-, =O (carboxylate)	H_2C — =O, NH_2	Complex kinetics, since it can technically be considered a terpolymerization; both r_{AAc} and r_{AAm} are similar and close to 1 [24]
pH > 6	H_2C — O^-, =O (carboxylate)	H_2C — =O, NH_2	Decreased r_{AAc}, increased r_{AAm}

For simplicity, we refer to the acidic monomers as AMPS and AAc throughout the paper, acknowledging the change in structure as we discuss experimental conditions (rather than in monomer name). However, based on the above discussion (and on the use of NaOH and NaCl for pH and salt adjustment, respectively), the monomers become sodium salts as the acids dissociate. This will be discussed in more detail in what follows. However, the presence of NaAMPS (2-acrylamido-2-methylpropane sulfonic acid sodium salt) and NaAAc (acrylic acid sodium salt or sodium acrylate) is implied as pH increases.

1.1.2 Effect of Ionic Strength

The polyelectrolyte nature of this terpolymer means that the ionic strength (IS) of the polymerizing mixture must also be considered. To minimize the repulsion between charges (both within the polymer chains and between the monomers and the chains), counter-ions can be added to the system in the form of salt. These counter-ions shield (and effectively neutralize) the charged molecules, which limits repulsion and increases reactivity. The IS of a given solution can be calculated according to Equation (2).

$$IS = \frac{1}{2} \sum c_i z_i^2 \tag{2}$$

where c_i is the molar concentration of ion i (mol/L) and z_i is the charge of ion i.

Not only does the ion charge number play a role in the ion shielding, but the type of cation does as well; this affects the electrostatic attraction between anions and counter-ions. It has been shown that the reactivities of both AAm and AAc in copolymerization can be affected by the type of cation [33]. In the current investigation, only NaCl is used to manipulate ionic strength, but extensions to other cations may be of interest.

Ionic strength effects have been evaluated for both acrylamide and acrylic acid homopolymerization kinetics, and have often been studied alongside pH effects (see, for example, [17,18,20]). As mentioned in the discussion surrounding pH, a smaller amount of information is available for the AMPS comonomer, since it is less widely used. However, since it

is a strong acid, it is expected that the terpolymerization of AMPS/AAm/AAc will also be influenced by the IS of the pre-polymerization mixture.

The effect of NaCl on polyacrylamide synthesis was studied by Lacik et al. [17] alongside their pH investigation. For aqueous polymerization with 5 wt% acrylamide, no change in k_p was observed over the range of 0.001 M to 0.1 M NaCl. Further increasing the NaCl concentration to 1 M resulted in a slight increase of k_p. The effect of NaCl (or other salt) addition on poly(acrylic acid) synthesis is much more pronounced, as the cations from the salt act as counter-ions, providing charge screening and increased reactivity as described previously. The impact of salt addition on poly(acrylic acid) kinetics was first described by Kabanov et al. [18], who described an "ion pair mechanism" that significantly increased the propagation rate and the molecular weights of the product polymers. Since then, similar ionic strength effects have been reported by many other groups for homopolymerization of acrylic acid and copolymerization of acrylic acid with acrylamide [7, 9, 20, 23, 24, 34].

Specifically, copolymerization studies for acrylamide/acrylic acid have shown that ionic strength affects the rate of polymerization and monomer reactivity ratios (see, for example, the recent study by Riahinezhad et al. [7]). When the acrylic acid monomer is partially or fully ionized, the reactivity ratio associated with AAc is low (due to charge repulsion). Experimental results have shown that adding salt (typically NaCl) to the pre-polymerization formulation can provide charge screening, thus increasing the incorporation of AAc (and r_{AAc}) [7, 9, 24].

1.1.3 Effect of Monomer Concentration

In aqueous polymerization, the total monomer concentration ([M]) can drastically affect the kinetics. This is especially true for polyelectrolytes, as the monomer concentration can also affect the ionic strength of the polymerizing mixture. The kinetic study for AMPS homopolymerization discussed earlier [25] compared rate constants (k_p and k_t) for aqueous solution polymerization (at 40°C) with 20 wt% AMPS (1.04 M) and 50 wt% AMPS (2.79 M). The analysis indicated that k_p was higher at a lower [M]; at the higher [M], a four-fold decrease in k_p was reported. In this case, Beuermann et al. [25] suggested that the reduction in k_p may be due to reduced chain mobility and repulsion between charged monomers and charges along the macroradical. Similar behavior has been observed for the homopropagation of acrylamide [17, 35], acrylic acid [36], and methacrylic acid [37-39].

The relationship between monomer concentration, ionic strength and polymerization kinetics studied for poly(methacrylic acid) [38] can provide insight about the poly(acrylic acid) case. Pulsed-laser polymerization results showed that k_p decreased with increasing [M] (as for the AMPS study) for the non-ionized case (α=0); there was a four-fold decrease as the concentration changed from 5 wt% (0.59 M) to 40 wt% (4.72 M). Conversely, for the fully ionized case (α=1), k_p increased with increasing monomer concentration (three-fold increase over the same range), which may be due to charge screening. In all cases (that is, at all monomer concentration levels), the k_p was higher for the non-ionized monomer than the ionized monomer [38]. This is as expected, since the ionized monomer will repel other monomers and charged macroradicals due

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to the like charges. Interestingly, polymerizations at lower monomer concentrations exhibited a more drastic change in k_p as the degree of ionization increased. That is, ionization effects were more pronounced at low monomer concentration. This may indicate that a higher monomer concentration (and, therefore, a higher ionic strength for the fully ionized case) stabilizes the system via charge screening.

As mentioned in the discussion of other recipe factor effects, extensions from homopolymerization to multi-component systems (copolymerization or terpolymerization) should be made with caution. The influence of monomer concentration on the copolymerization kinetics of AAm/AAc has been studied recently [8, 9, 24]. In general, copolymerization studies have shown that increased [M] does not have an isolated effect; it is influenced by other factors including pH and ionic strength (as one might expect given the complexity of the system). Riahinezhad et al. [8] reported that the effect of [M] becomes more pronounced at higher pH levels (that is, partially or fully ionized conditions); changing [M] at pH 3 had almost no effect on the reactivity ratios, but had significant effects at pH 7. At higher pH levels, increasing [M] results in a decreased r_{AAm} and an increased r_{AAc}. These results agreed with those reported previously by Rintoul and Wandrey [24]. Riahinezhad et al. [8] also observed that an increase in monomer concentration made reactivity ratios less "scattered" (that is, more consistent over different pH levels). This observation aligns with the stability observed in the poly(methacrylic acid) study described previously [38]; higher monomer concentration seems to provide additional charge screening, thus decreasing the effect of monomer ionization on polymerization kinetics.

It is well-known, but worth acknowledging nonetheless, that adjusting monomer concentration can also have a significant impact on the molecular weight of the polymer product. Molecular weight is directly proportional to [M], which provides researchers with a convenient way to achieve the desired molecular weight for a custom terpolymer.

1.2 Terpolymer Properties of Interest

For the current study, the target application for AMPS/AAm/AAc terpolymers is enhanced oil recovery (EOR). Polyacrylamide-based materials are often used for EOR but are known to degrade at the high temperatures and pressures that are characteristic of oil reservoirs. Previously, it has been suggested that by adding AMPS to an AAm/AAc polymer, the bulky sulfonic acid group will protect the main chain (due to steric hindrance) and increase viscosity [1, 40]. Also, strong hydrogen bonding will increase the polymer's solubility in water. Recent studies have also shown that copolymers containing AMPS are more stable in conditions of high temperature and high salinity [40, 41].

1.2.1 Ternary Reactivity Ratios

One must first establish the reactivity ratios for the system to predict terpolymer composition and the resulting terpolymer microstructure. Reactivity ratios provide information about the degree of incorporation of each comonomer into the resulting polymer and can be estimated by applying the error-in-variables method to experimental data (namely, conversion, initial composition and cumulative terpolymer composition). The importance of using appropriate

estimation techniques has been strongly emphasized in previous work; specific details about ternary reactivity ratio estimation can be found in recent work by Scott and Penlidis [11].

1.2.2 Cumulative Terpolymer Composition

A significant advantage of using terpolymers in EOR is the ability to tailor the product for the application requirements. Terpolymers can incorporate the desirable properties of several components simultaneously, which ultimately improves the overall performance of the polymer [42]. The proportions of comonomers to be included in the recipe can be selected based on the expected degree of incorporation (that is, reactivity ratio estimates) and the known properties of their specific end groups. For example, high levels of amide groups are known to increase stability, while high levels of carboxylate ions will increase viscosity and decrease adsorption in the reservoir [43].

During AAm/AAc copolymer design work by Riahinezhad et al. [44], high levels of acrylamide showed the best performance for the EOR application. When the fraction of acrylamide was between 65% and 95%, the product exhibited high molecular weights and high shear viscosity (with maximum shear viscosity observed at 70% AAm) [45], both characteristics being desirable in EOR. The same study found that small amounts of acrylic acid improved the polyelectrolyte nature of the copolymer, but too much AAc resulted in brine sensitivity.

These considerations can be extended to the case of the AMPS/AAm/AAc terpolymer. We expect that high levels of acrylamide will still be necessary, therefore preference should be given to solution conditions that promote high AAm incorporation into the product terpolymer. Ideally, we are also looking for conditions where the terpolymerization exhibits very little composition drift, so that the cumulative terpolymer composition remains approximately constant at any level of conversion.

1.2.3 Terpolymer Microstructure

Knowledge of the terpolymerization reactivity ratios also provides information about the terpolymer microstructure, namely sequence length distribution and triad fractions. In some cases, two copolymers may have the same cumulative composition, but the distribution of the comonomers (and therefore functional groups) along the polymer backbone may differ. The structure of the copolymer (block, alternating, random, etc.) affects its viscoelastic properties (consider chain flexibility, for example), and will also affect the charge density in polyelectrolytes. For enhanced oil recovery, the microstructure can significantly affect the conformation of polymer chains in solution (that is, coiling or uncoiling). Since conformation affects the solution viscosity and EOR sweep efficiency, the distribution of the acidic comonomers is an important design consideration.

Sequence length distribution can be evaluated using probability functions, given the reactivity ratios and the composition of the polymerizing mixture [46]. The three-component case is presented in Equation (3), but the concept can be extended to any number of comonomers.

$$p_{ii} = \frac{f_i}{f_i + \frac{f_j}{r_{ij}} + \frac{f_k}{r_{ik}}} = \frac{r_{ij}r_{ik}f_i}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k} \tag{3a}$$

$$p_{ij} = \frac{r_{ik}f_j}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k} \tag{3b}$$

$$p_{ik} = \frac{r_{ij}f_k}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k} \tag{3c}$$

Where p_{ij} represents the probability that a growing radical ending with unit i adds monomer j.

Alternatively, terpolymer microstructure can be quantified using instantaneous triad fractions, A_{ijk}. These values are also statistically based and can be calculated as a function of feed composition, given the associated reactivity ratios (see Equation (4)). Note that only the i-centered triads are presented in the equations, but the expressions can easily be extended to j- and k- centered triads (thus, there are 18 possible triad fractions for the terpolymer system).

$$A_{iii} = p_{ii}^2 = \left(\frac{r_{ij}r_{ik}f_i}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right)^2 \tag{4a}$$

$$A_{jij} = p_{ij}^2 = \left(\frac{r_{ik}f_j}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right)^2 \tag{4b}$$

$$A_{kik} = p_{ik}^2 = \left(\frac{r_{ij}f_k}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right)^2 \tag{4c}$$

$$A_{iij} = A_{jii} = p_{ii}p_{ij} = \left(\frac{r_{ij}r_{ik}f_i}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right)\left(\frac{r_{ik}f_j}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right) \tag{4d}$$

$$A_{iik} = A_{kii} = p_{ii}p_{ik} = \left(\frac{r_{ij}r_{ik}f_i}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right)\left(\frac{r_{ij}f_k}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right) \tag{4e}$$

$$A_{jik} = A_{kij} = p_{ij}p_{ik} = \left(\frac{r_{ik}f_j}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right)\left(\frac{r_{ij}f_k}{r_{ij}r_{ik}f_i + r_{ik}f_j + r_{ij}f_k}\right) \tag{4f}$$

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While these calculations are theoretical in nature, previous research has shown promising agreement between predicted triad fractions and experimental results from ^{13}C NMR [47].

1.2.4 Terpolymer Molecular Weights

High molecular weight polymers increase the solution viscosity and the permeability reduction factor (that is, the ability for EOR polymers to adsorb onto the porous well walls, reducing channeling effects and increasing sweep efficiency). This means that high molecular weight polymers allow more of the reservoir to be exposed to the displacing fluid and less oil is left behind [43]. The increased viscosity and permeability reduction factor both increase the oil recovery factor (compared to the same amount of a lower molecular weight polymer), which means that a high molecular weight polymer solution requires less polymeric material to achieve a designated recovery factor. The advantage of using less polymeric material in the EOR process is evident, both in terms of environmental and economic implications.

If the molecular weights are too high, there will be additional complications associated with the EOR application. One of the major issues is the potential degradation of the polymer, as high molecular weight chains tend to be more shear sensitive (especially in typical EOR conditions). Another concern is that the viscosity of the polymer flooding solution may end up being too high; this could lead to problems with reduced injectivity (where injectivity is the ratio between injection rate and pressure drop) and slower fluid throughput in the reservoir (largely due to plugging) [48].

Therefore, molecular weight control is important during the design and synthesis of EOR polymers. In free radical polymerization, the molecular weight can be controlled through careful selection of monomer concentration and feed composition (in the multicomponent case); chain-transfer agents may also be used. Most researchers studying acrylamide-based polymers for enhanced oil recovery agree that a target molecular weight on the order of 10^6 g/mol is appropriate [1, 44, 49].

2. EXPERIMENTAL

2.1 Materials

Monomers 2-acrylamido-2-methylpropane sulfonic acid (AMPS; 99%), acrylamide (AAm; electrophoresis grade, 99%), and acrylic acid (AAc; 99%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). AAc was purified via vacuum distillation at 30°C, while AAm and AMPS were used as received. Initiator (4,4'-azo-bis-(4-cyanovaleric acid), ACVA), inhibitor (hydroquinone) and sodium hydroxide were also purchased from Sigma-Aldrich. Sodium chloride from EMD Millipore (Etobicoke, ON, Canada) was used as received. In terms of solvents, water was Millipore quality (18 MΩ·cm); acetone (99%) and methanol (99.8%) were used as received. Nitrogen gas (4.8 grade) used for degassing solutions was purchased from Praxair (Mississauga, ON, Canada).

2.2 Polymer Synthesis

In general, the experimental techniques described by Riahinezhad et al. [6] were adopted for these terpolymer systems. As per the EVM design of experiments procedure for terpolymerizations [12], each pre-polymerization recipe is rich in one comonomer ($f_{AMPS,0}$/$f_{AAm,0}$/$f_{AAc,0}$ = 0.8/0.1/0.1, 0.1/0.8/0.1, 0.1/0.2/0.7). Prior work has shown poor polymerization when the AAc fraction is too high [26], therefore the constrained design shown in Figure 1 is used for the current experimental work. Additional experimental conditions (at each of these feed compositions) are described in what follows.
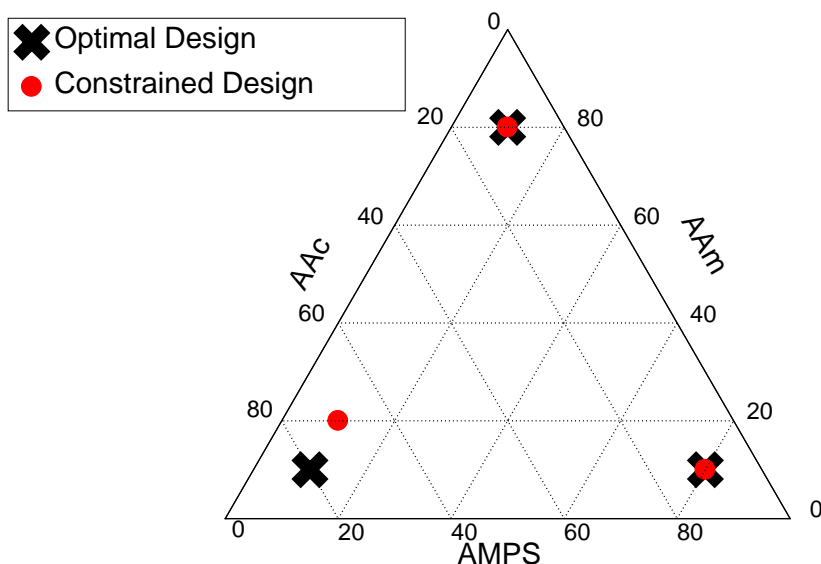

FIGURE 1: Error-in-Variables Model Design of Experiments for Reactivity Ratio Estimation
(Constrained Design for Terpolymerization)

Solutions to be polymerized were prepared with target monomer concentrations (according to the experimental design of Table 2) and the initiator (ACVA) concentration was adjusted to maintain a constant $[M]/[I]^{1/2}$ ratio (=15.8). Prior to polymerization, solutions were titrated with

sodium hydroxide to adjust the solution to the desired pH (±0.5), and sodium chloride was added to adjust ionic strength among the experiments.

All solutions were purged for two hours under 200 mL/min nitrogen. After degassing, aliquots of ~20 mL of solution were transferred to sealed vials using the cannula transfer method. Free-radical solution (aqueous phase) polymerizations were run in a temperature-controlled shaker-bath (OLS200; Grant Instruments, Cambridge, UK) at 40°C and 100 rpm. Vials were removed at selected time intervals, placed in ice and further injected with approximately 1 mL of 0.2 M hydroquinone solution to stop the polymerization. Polymer samples were isolated by precipitating the products in acetone, filtered (paper filter grade number 41, Whatman; Sigma-Aldrich, Oakville, ON, Canada) and vacuum dried for 1 week at 50°C.

Solution properties, namely, pH, ionic strength and monomer concentration are expected to affect the polymerization kinetics and resulting terpolymer properties. Therefore, in our prior work [5], all variables were kept constant and controlled to the extent possible. In contrast, the current work employs a definitive screening design (using Design Expert software) to adjust four variables (in 3 levels each) simultaneously and glean general information about the system. Level selection was informed by prior work (for the AAm/AAc copolymer [7, 8] and the AMPS/AAm/AAc terpolymer [5]) and influenced by considering desirable properties for enhanced oil recovery application performance [44]. The definitive screening design is presented in Table 2 (Runs #1 through #9). The conditions for two additional runs (Runs #10 and #11) were informed by

preliminary results and kept screening variables constant to the extent possible, for comparison purposes.

TABLE 2: Definitive Screening Design for Terpolymerization of AMPS/AAm/AAc

Run #	pH	IS	[M]	Feed Composition ($f_{AMPS,0}$/$f_{AAm,0}$/$f_{AAc,0}$)
1	7	1.5 M	1.0 M	0.1/0.2/0.7
2	5	1.2 M	1.0 M	0.8/0.1/0.1
3	7	1.8 M	1.5 M	0.8/0.1/0.1
4	7	1.2 M	0.5 M	0.1/0.8/0.1
5	9	1.2 M	1.5 M	0.1/0.2/0.7
6	5	1.8 M	0.5 M	0.1/0.2/0.7
7	9	1.8 M	1.0 M	0.1/0.8/0.1
8	5	1.5 M	1.5 M	0.1/0.8/0.1
9	9	1.5 M	0.5 M	0.8/0.1/0.1
10	7	1.5 M	1.0 M	0.8/0.1/0.1
11	7	1.5 M	1.0 M	0.1/0.8/0.1

By combining the definitive screening design with optimal feed compositions (as per the EVM design of experiments for ternary reactivity ratio estimation; recall Figure 1), we can analyze different subsets of data for parameter estimation under specific conditions. For example, from Table 2, we could use Runs #1, #3 and #4 to estimate (approximate) reactivity ratios for pH 7. Although [M] and IS are varying, the associated feed compositions for these 3 runs make up an optimal design. Therefore, full conversion data from 3 runs can be used for parameter estimation. It is important to note that these parameter estimates are general; reactivity ratios from these experiments should not be used to predict cumulative terpolymer composition or terpolymer microstructure. Rather, these screening runs can be used to examine how changes in pH, ionic

strength and monomer concentration affect general trends (i.e. incorporation of various comonomers, rate of polymerization, molecular weight averages, and so on). These trends inform subsequent runs, with the intent to manipulate pre-polymerization recipes and terpolymerization kinetics to create custom-made materials.

2.3 Characterization

Conversion of all polymer samples was determined using gravimetry. Due to the high ionic strength (and necessarily high salt content), we observed that sodium chloride remained present in the polymer samples at an approximate 1:1 ratio with acrylamide. This was initially deduced from elemental analysis results and uncharacteristically high conversion measurements, and then independently confirmed for select samples via inductively coupled plasma mass spectrometry (ICP). As per the recommendation of Riahinezhad et al. [7], the mass of the sodium ions (attracted to the dissociated acids along the polymer chain) was considered in conversion calculations.

Molecular weight averages were determined using gel permeation chromatography (PL-GPC 50, Agilent, with two columns, type PL aquagel-OH MIXED-H 8 µm, Agilent). In this study, four detectors were employed: refractive index, low-angle and right-angle light scattering (LALLS/RALLS), and differential pressure. To minimize the charge interactions between the column and the polymer samples, a buffer solution of pH 7 was used as the mobile phase (flowing at a rate of 1.0 mL/min). The buffer was prepared using sodium nitrate (0.2 M) and sodium

phosphate (monobasic and dibasic, 0.1 M). The synthesized polymers were dissolved in the mobile phase (pH 7 buffer) to obtain concentrations of ~1 mg/mL; prior to injection, polymer solutions were filtered through a 0.2 μm filter. Polyacrylic acid – sodium salt calibration standards were obtained from Agilent Technologies and their peak average molecular weight ($\overline{M}_p$) values ranged from 4.67×10^5 to 2.25×10^6 g/mol. Calibration was also confirmed using a well-characterized copolymer (poly(acrylamide-co-acrylic acid) partial sodium salt from Aldrich) and measurements were in good agreement with the expected results (coefficient of variation <10% for both $\overline{M}_w$ and $\overline{M}_n$).

Polymer composition was measured using elemental analysis (CHNS, Vario Micro Cube, Elementar). The content of elemental C, H, N and S in the samples was determined. Calculation of the terpolymer composition did not include H measurements, as residual water has been known to affect the determined H content.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

As mentioned in Section 1.1.1, changes in solution pH affect the degree of dissociation (and therefore the charge) of acidic monomers and the resulting polymer. By grouping the screening experiments according to pH level (that is, pH level constant with varying ionic strength and monomer concentration), we can estimate ternary reactivity ratios at each pH level. The

screening runs (from Table 2) used for each analysis and the resulting reactivity ratio estimates (obtained using full conversion data and cumulative terpolymer composition to obtain ternary reactivity ratios) are shown in Table 3. Again, note that at each pH, there is a pre-polymerization recipe rich in each of the three comonomers. For all estimation steps, preliminary estimates were taken from recent work by our group [5]; in all cases, monomer 1 is 2-acrylamido-2-methylpropane sulfonic acid (AMPS), monomer 2 is acrylamide (AAm) and monomer 3 is acrylic acid (AAc).

TABLE 3: pH Effects on Ternary Reactivity Ratio Estimates for AMPS/AAm/AAc ($M_1/M_2/M_3$)

pH	Data from Run #	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
5	2, 6, 8	0.96	0.53	0.25	1.22	1.55	0.51
7	1, 3, 4	1.14	0.66	0.45	0.99	1.48	0.42
9	5, 7, 9	1.12	0.53	0.32	1.56	2.07	0.55

The estimation results at varying pH levels do not show any clear correlation between pH and reactivity ratio estimates; most values for a given parameter (say r_{ij}; "vertical" comparison within Table 3) are close together. However, the point estimates only provide part of the story. We can also examine the joint confidence regions (JCRs, or error ellipses) for the parameter estimates, which provide additional information about possible parameter correlation and degree of confidence for each estimate. JCRs for all three pH levels and all ternary reactivity ratio pairs are presented in Figure 2.
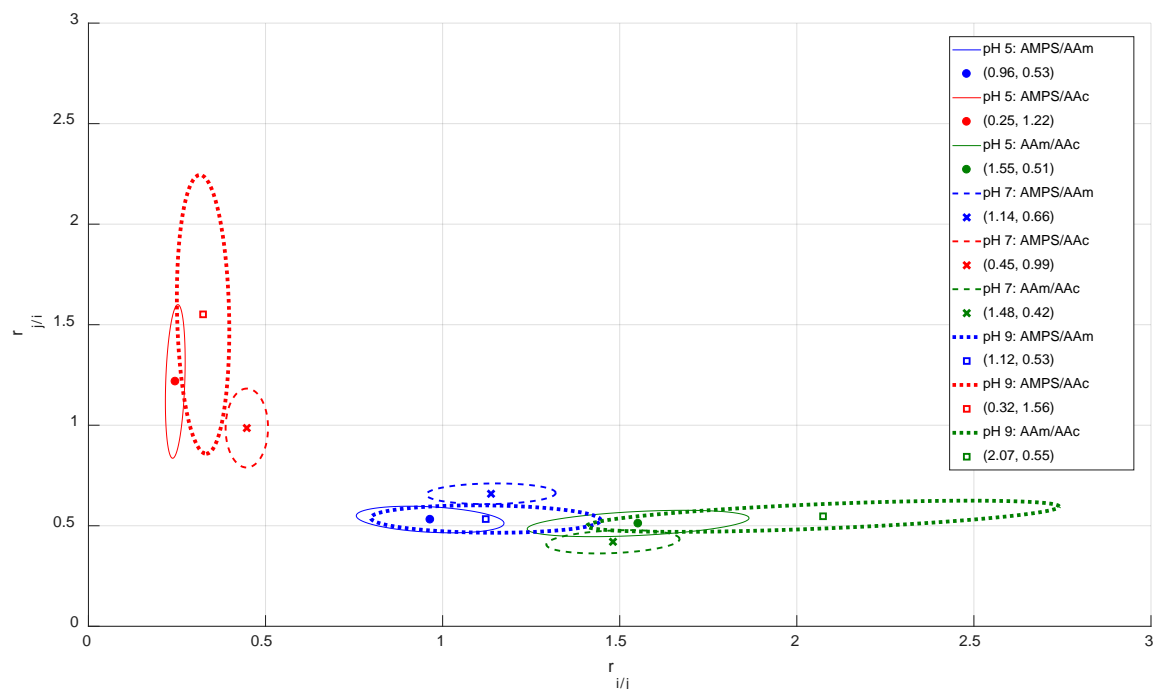
FIGURE 2: Comparison of Reactivity Ratio Estimates for AMPS/AAm/AAc at pH 5, 7 and 9

Figure 2 provides significantly more information than the numerical estimates of Table 3. First, we can evaluate the area of the JCRs associated with each pH level. At pH 5 and pH 7, the JCRs are small, which indicates a high degree of confidence in the estimates. At pH 9, the JCRs are larger, which suggests more uncertainty. This may be related to the fact that other variables (namely ionic strength and monomer concentration) are not held constant, which affects the precision of the parameter estimates. Alternatively, fewer data points are available for Run #9 as it had an unusually long induction time, so the parameters are being estimated from a smaller (and therefore less informative) data set.

A second observation from Figure 2 is related to the overlap in JCRs, especially for the AMPS/AAm and AAm/AAc comonomer pairs. This agrees with the numerical results shown in Table 3, which

indicate that most parameter estimates are close together. According to Figure 2, there is no statistically significant difference between parameter estimates for the AMPS/AAm and AAm/AAc comonomer pairs at pH 5 and pH 9. Distinct JCRs (that is, without overlap) are visible for the AMPS/AAc copolymer pair, which suggests that the acidic comonomers may be more affected by changes in pH. This agrees with physico-chemical expectations, as the degree of acid dissociation is likely to be influential in the pH range being studied.

Given prior investigations of pH effects (especially for the AAm/AAc copolymer [8, 22-24]), one might expect bigger differences in the reactivity ratios at different pH levels. However, it is important to keep in mind that these results are under specific conditions, where several variables are being manipulated simultaneously. pH effects are largely due to acid dissociation and charge effects. Therefore, adding sodium chloride to the recipe (to adjust ionic strength) increases charge screening, reducing acrylic acid repulsion and moderating the effect that a pH increase would have in isolation.

The final takeaway from Figure 2 is the shape and orientation of the JCRs. All JCRs are somewhat "stretched" in one direction, which indicates more uncertainty associated with one of the parameters. This phenomenon has been described in our recent work [50] and is likely related to the absolute value of the parameter estimate; a larger absolute value results in more uncertainty. It is also important to note that the JCRs are either horizontal or vertical (not on a diagonal). This indicates that parameter correlation is minimal, thanks to well-designed experimental runs based on the error-in-variables model.

As we refer again to the numerical estimates of Table 3, it is interesting to note that at each pH level, the relationship between reactivity ratios for a given comonomer pair remains consistent. That is, for any subset of screening runs, $r_{12} > r_{21}$, $r_{13} < r_{31}$ and $r_{23} > r_{32}$. Therefore, regardless of pH, the degree of incorporation of each comonomer remains relatively constant. This is confirmed by using the reactivity ratio estimates from Table 3 to predict the cumulative terpolymer composition at pH 5, pH 7 and pH 9 given the AAm-rich recipe ($f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.1/0.8/0.1); see Figure 3.
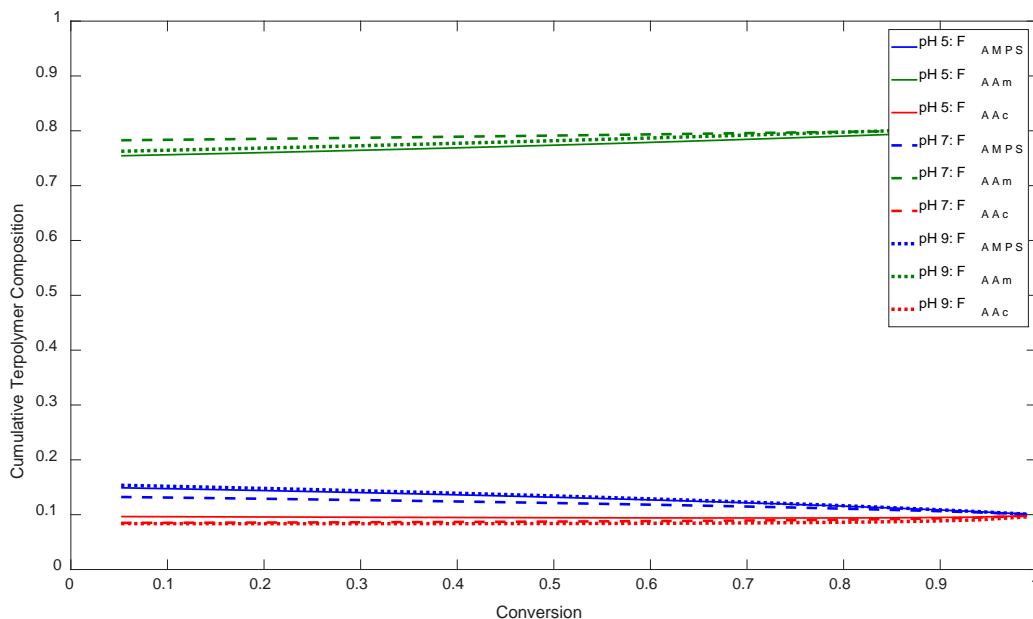

FIGURE 3: Predicted Cumulative Composition from Screening Experiments for AAm-rich Terpolymer at pH 5, 7 and 9

The relationship between reactivity ratios for comonomer pairs becomes even more interesting when we compare the experiment results to the (previously determined [5]) preliminary

estimates. Scott et al. [5] estimated ternary reactivity ratios for AMPS/AAm/AAc using data collected at pH 7, with constant ionic strength (IS = 0.9 M) and monomer concentration ([M] = 1.0 M). Therefore, we can easily compare two sets of reactivity ratios from data obtained at pH 7: the current estimates (with varying IS and [M]) versus earlier estimates (with constant IS and [M]).

TABLE 4: Reactivity Ratio Estimates at pH 7 with Varying and Constant IS and [M]

Experimental Conditions	r_{12}		r_{21}	r_{13}		r_{31}	r_{23}		r_{32}
Current study: pH 7 1.2 M < IS < 1.8 M 0.5 M < [M] < 1.5 M	1.14	>	0.66	0.45	<	0.99	1.48	>	0.42
Scott et al. [5]: pH 7 IS = 0.9 M [M] = 1.0 M	0.66	<	0.82	0.82	>	0.61	1.61	>	0.25

The key takeaway from Table 4 is the shift in relationship for two of the comonomer pairs. As discussed previously, the current experimental results indicate that $r_{12} > r_{21}$ and $r_{13} < r_{31}$ in all cases (recall Table 3). In contrast, the reactivity ratio estimates determined by Scott et al. [5] show the opposite: $r_{12} < r_{21}$ and $r_{13} > r_{31}$. Since the pH is the same for these two data sets, we can conclude that this "cross-over" behavior is not a result of pH effects. The most significant difference (aside from varying IS and [M] vs. constant IS and [M]) is the increased ionic strength used in the current experiments. Therefore, we are further motivated to investigate the effects of ionic strength on ternary reactivity ratios of AMPS/AAm/AAc (see Section 3.2). Specifically, if

we can learn more about how ionic strength creates a cross-over point (at which $r_{ij} \approx r_{ji}$), we can target specific reaction conditions to create custom-made materials with desirable properties.

Specifically, the following remarks can be made:

(1) No clear correlation exists between pH and reactivity ratio estimates for the range of 5 to 9.

(2) The largest JCRs (and therefore the most uncertainty) were observed for reactivity ratio estimation at pH 9.

(3) Acidic comonomers (AMPS and AAc) seem to be more affected by changes in pH.

(4) pH effects are likely masked by salt addition in this type of screening design.

(5) Well-designed experiments (using the error-in-variables model) minimize parameter correlation.

(6) Cross-over behavior was observed for AMPS/AAm and AMPS/AAc comonomer pairs (current designs vs. Scott et al. [5]); both data sets are at pH 7, therefore cross-over behavior is due to some other factor effect.

3.2 Effect of Ionic Strength

Ionic strength is an important factor to consider during the synthesis of polyelectrolytes. As discussed in Section 1.1.2, adding counter-ions (in the form of salt) to a pre-polymerization solution can reduce repulsion between charged monomers and polymer chains. This effectively neutralizes the charged molecules (dissociated AMPS and/or acrylic acid, in this case), which minimizes repulsion and increases the rate of polymerization.

The design of experiments used requires that the "low" (-1) level for ionic strength be 1.2 M. This is the result of high monomer concentration and a high proportion of acidic monomer in a "low" ionic strength run. Specifically, in Run #5 (from Table 2), a total monomer concentration of 1.5 M and full dissociation of AMPS and AAc comonomers result in an ionic strength of 1.2 M before any NaCl is added to the recipe. Therefore, the "low" (-1) ionic strength level is necessarily 1.2 M. This imposes a relatively high range for the ionic strength investigation, but this is a consequence of using the specific experimental design for such a complex polymerization, yet in methodical steps.

The data from the experiments were now grouped according to ionic strength for reactivity ratio estimation. As explained previously, ternary reactivity ratios were estimated for the AMPS/AAm/AAc terpolymer at each ionic strength level (with varying pH and monomer concentration). The trials used for each analysis and the resulting reactivity ratio estimates (obtained as described in Section 3.1) are shown in Table 5.

Table 5: Ionic Strength (IS) Effects on Ternary Reactivity Ratio Estimates for AMPS/AAm/AAc ($M_1/M_2/M_3$)

IS	Data from Run #	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
1.2 M	2, 4, 5	0.90	0.65	0.24	1.08	1.87	0.52
1.5 M	1, 8, 9	13.19	0.68	0.48	27.02	7.47	0.70
1.8 M	3, 6, 7	1.11	0.54	0.46	1.35	1.65	0.55

Given the reactivity ratios estimated at all three ionic strength levels, there is an obvious difference at IS = 1.5 M. For each reactivity ratio pair at IS = 1.5 M, the larger parameter estimates (namely r_{12}, r_{31} and r_{23}) are much larger than under the other conditions. These values have likely been overestimated (due to more uncertainty associated with these parameters), and the JCRs will be examined to troubleshoot this aspect (see Figure 4). Inaccurate estimation may be due to the effects of non-constant pH and monomer concentration, or (as suggested for the pH 9 analysis, see Section 3.1) non-informative experimental data.

(a)

(b)
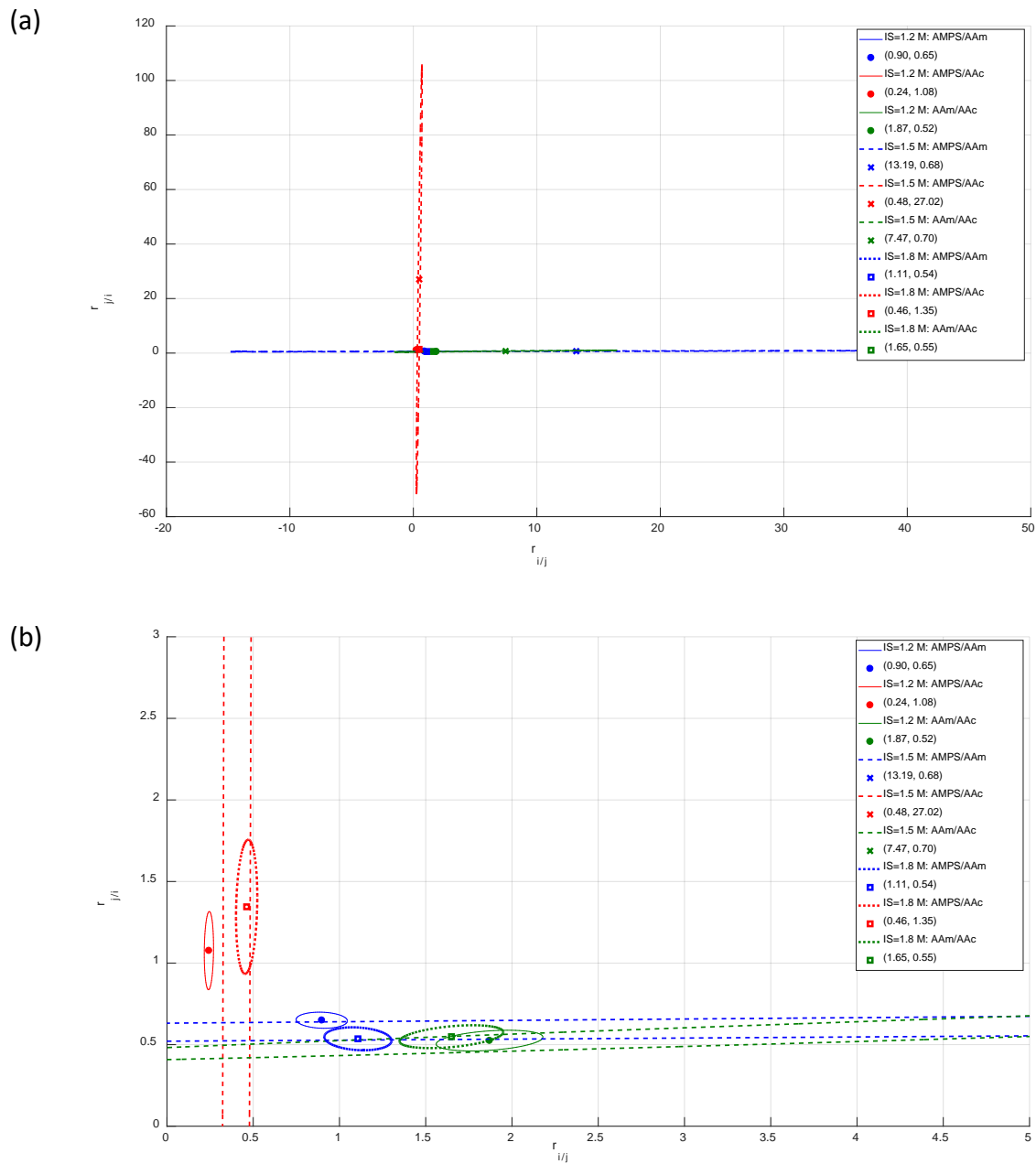
FIGURE 4: Comparison of Reactivity Ratio Estimates for AMPS/AAm/AAc
at IS = 1.2 M, IS = 1.5 M and 1.8 M ((a) All Data and (b) Without the IS = 1.5 M Data)

Examining the point estimates and joint confidence regions for these reactivity ratios confirms

that there is substantial uncertainty for the IS = 1.5 M data. These long and narrow JCRs

emphasize the uncertainty associated with r_{12}, r_{31} and r_{23}; since the error is associated with all

three comonomers, parameter estimates can likely be improved by eliminating the confounding variables (that is, keeping pH and [M] constant during synthesis). If the uncertainty were related to non-informative data or poor experimental design, we would expect the error to be more clearly associated with one specific comonomer.

3.2.1 Ternary Reactivity Ratios for Constant pH and [M]

The most likely cause for the error associated with IS = 1.5 M is the influence of changing pH and [M]. Consideration of non-constant variables is a necessary part of screening design analysis, but it seems that some combinations of runs are more prone to error (that is, more influenced by non-constant variables) than others. Therefore, for improved reactivity ratio estimates at IS = 1.5 M, two supplemental runs were added to the experimental docket: Runs #10 and #11 (recall Table 2). Both runs are informed by the EVM design of experiments for ternary reactivity ratio estimation and vary only in feed composition. The data from these runs can be combined with the data from Run #1 for accurate ternary reactivity ratio estimation at IS = 1.5 M, pH 7 and [M] = 1.0 M. As an additional bonus, these runs are under similar conditions to some of our previous work; Scott et al. [5] have reported ternary reactivity ratios for AMPS/AAm/AAc from data collected at IS = 0.9 M, pH 7 and [M] = 1.0 M. Therefore, comparison of reactivity ratios can be performed for IS = 0.9 M and IS = 1.5 M, all else being equal.

First, we return to the data from Runs #1, #10 and #11 to estimate reactivity ratios at IS = 1.5 M. As before, full conversion data can be analyzed using the cumulative composition model. The

point estimates here are much more reasonable (compared to the IS = 1.5 M results of Table 5) and the JCR areas have decreased significantly (see Figure 5). This confirms that controlling IS, pH and [M] gives more reliable parameter estimates.
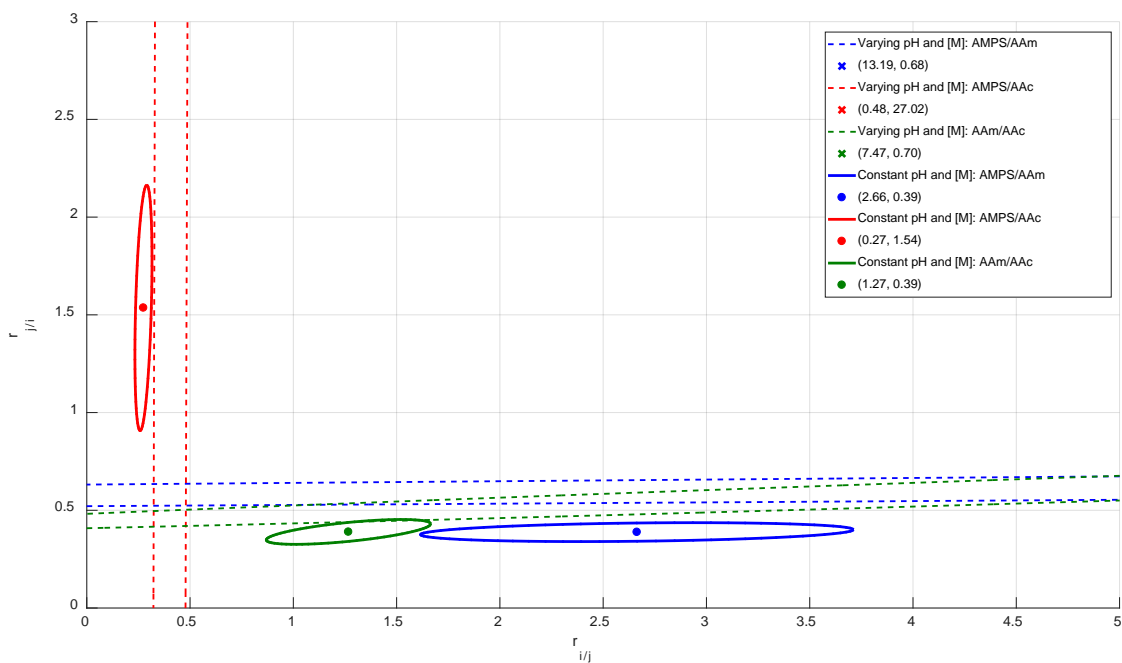

FIGURE 5: Reactivity Ratio Estimates for AMPS/AAm/AAc at IS = 1.5 M;
Comparison of Results at Constant/Varying pH and [M]

TABLE 6: Reactivity Ratio Estimates at IS = 1.5 M with Varying and Constant pH and [M]

Experimental Conditions	r_{12}		r_{21}	r_{13}		r_{31}	r_{23}		r_{32}
IS = 1.5 M 5 < pH < 9 0.5 M < [M] < 1.5 M Data from Run #: 1, 8, 9	13.19	>	0.68	0.48	<	27.02	7.47	>	0.70
IS = 1.5 M pH = 7 [M] = 1.0 M Data from Run #: 1, 10, 11	2.66	>	0.39	0.27	<	1.54	1.27	>	0.39
IS = 0.9 M pH = 7 [M] = 1.0 M Data from Scott et al. [5]	0.66	<	0.82	0.82	>	0.61	1.61	>	0.25

Aside from the improved degree of confidence associated with the parameter estimates, we are also able to compare ternary reactivity ratios at IS = 1.5 M (current study) to IS = 0.9 M (Scott et al. [5]), with constant pH and monomer concentration. This comparison, shown in the last two rows of Table 6, provides an interesting result: we see the same change in relationship for the AMPS/AAm and the AMPS/AAc comonomer pairs that was observed during the pH analysis (recall the comparison between screening experiments and preliminary estimates in Section 3.1). The cross-over behavior observed for AMPS/AAm and for AMPS/AAc between IS = 0.9 M and IS = 1.5 M must be a result of changing ionic strength; all other variables are controlled. To find the true cross-over point (that is, the ionic strength at which r_{12} = r_{21} and r_{13} = r_{31}), additional experiments would need to be performed for 0.9 M < IS < 1.5 M at pH 7 and [M] = 1.0 M. However, this result proves that ionic strength in this range can be manipulated to adjust these reactivity ratios, thus improving control over the degree of incorporation of each comonomer in the product terpolymer. Interestingly, only the comonomer pairs containing AMPS exhibit cross-

over behavior in this range. Therefore, it is only possible to manipulate relationships between AMPS/AAm and AMPS/AAc by adjusting ionic strength. Cross-over behavior for the AAm/AAc comonomer pair has not been observed under current conditions, but has been observed for the analogous AAm/AAc copolymer by Riahinezhad et al. [8], Cabaness et al. [22] and Rintoul and Wandrey [24]. The crossover point varies slightly from study to study, but ranges from pH 3.77 to pH 5. In all cases, $r_{AAm} > r_{AAc}$ above the crossover point, but $r_{AAm} < r_{AAc}$ in more acidic solutions. It is unwise to make extensions directly from the copolymer case to the terpolymer case [11], but terpolymer synthesis below pH 5 might reveal the AAm/AAc cross-over point. One could conceivably manipulate both solution pH and IS to exploit this cross-over behavior, in order to influence reactivity ratio ranges for AMPS/AAm/AAc terpolymerization.

3.2.2 Cumulative Terpolymer Composition

The change in reactivity ratio estimates (as ionic strength increases) can directly influence cumulative terpolymer composition. As an example, refer to the final two rows of Table 6. We see that as ionic strength increases, both r_{21} and r_{23} decrease (from 0.82 to 0.39 and from 1.61 to 1.27, respectively). Physically, this suggests that the likelihood of acrylamide incorporation decreases as ionic strength increases; higher ionic strength (that is, more NaCl added) results in more charge screening, improving incorporation of the charged (acidic) monomers and reducing the incorporation of the acrylamide monomer.

We can confirm this observation by predicting cumulative terpolymer composition under different experimental conditions. Given ternary reactivity ratio estimates and initial feed compositions, we can use the recast Alfrey-Goldfinger model [51] to predict cumulative terpolymer composition as a function of conversion. As seen in Figure 6 and Figure 7, we can compare the cumulative composition of different terpolymers of AMPS/AAm/AAc, given reactivity ratios estimated at IS = 0.9 M and IS = 1.5 M. Experimentally speaking, pH and [M] were controlled at 7 and 1.0 M, respectively. Therefore, any changes in composition are primarily due to changes in ionic strength.
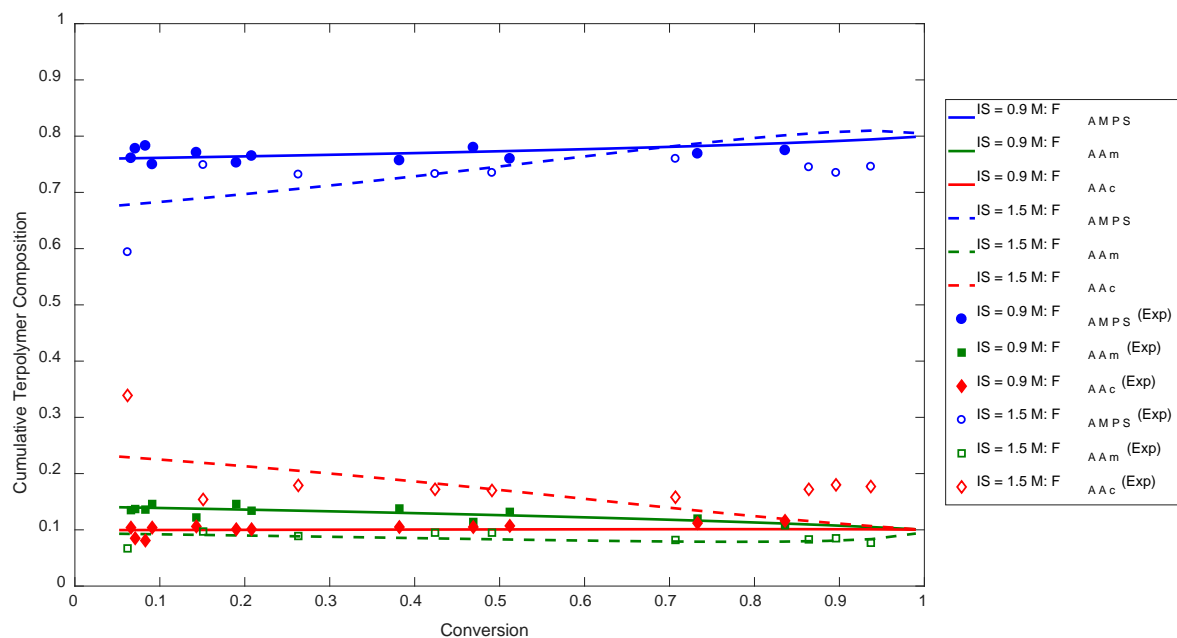
FIGURE 6: Cumulative Composition for AMPS-rich Terpolymer at IS = 0.9 M and 1.5 M

The predicted cumulative composition profiles (confirmed with experimental data) in Figure 6 reveal an important result. As ionic strength changes, the composition of the resulting terpolymer

changes substantially. For IS = 0.9 M, $\overline{F}_{AAm} > \overline{F}_{AAc}$, but for IS = 1.5 M, $\overline{F}_{AAm} < \overline{F}_{AAc}$. This agrees

with what we observed when evaluating the reactivity ratios: higher ionic strength creates charge

screening, reducing repulsion of the charged acrylic acid monomers. Therefore, an increased

acrylic acid incorporation and a decreased acrylamide incorporation is visible. This is especially

obvious for the AMPS-rich polymer, as the EVM-based design of experiments dictates an initial

feed composition of $f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.8/0.1/0.1. An equimolar concentration for AAm and

AAc (at least initially) emphasizes the fact that solution properties affect the degree of

incorporation of each comonomer.

To confirm that the increased ionic strength is reducing the acrylamide content in the product

terpolymer, we can also examine the acrylamide-rich terpolymer recipe. As shown in Figure 7,

the cumulative mole fraction of AAm in the product terpolymer is significantly reduced at IS = 1.5

M, especially at low conversion. Since high acrylamide content and minimal composition drift are

both desirable properties for the EOR application, solutions with lower ionic strength (IS = 0.9 M)

seem like the more promising candidate for synthesizing AMPS/AAm/AAc terpolymers
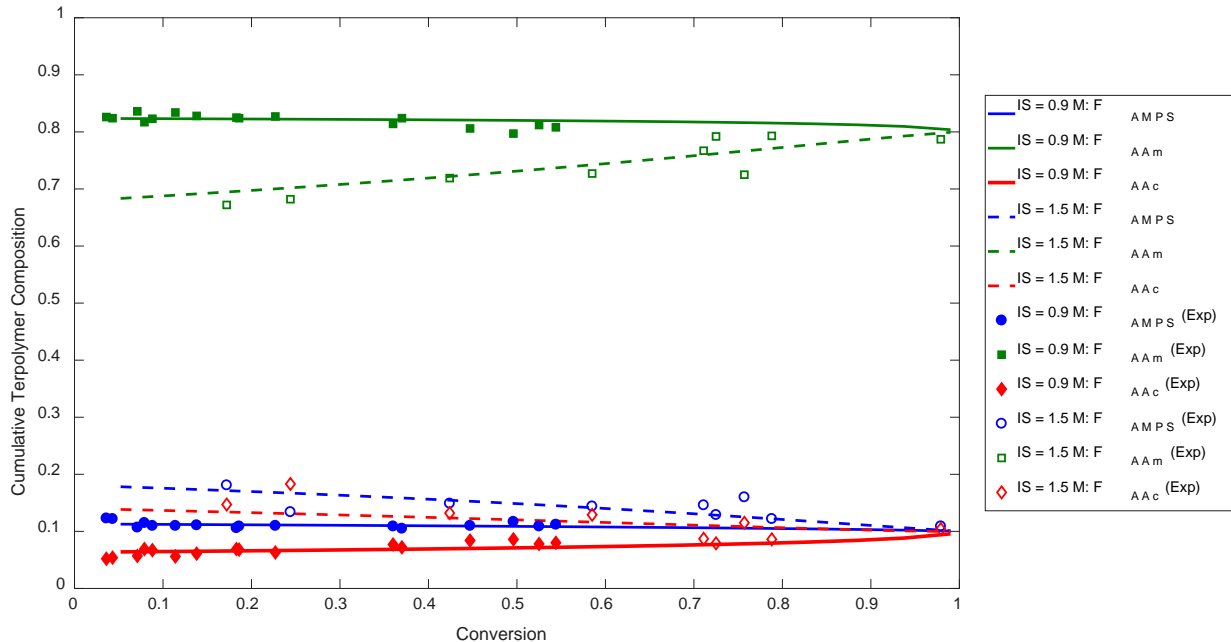
specifically for EOR.

FIGURE 7: Cumulative Composition for AAm-rich Terpolymer at IS = 0.9 M and 1.5 M

Before we conclude the discussion about the effect of ionic strength on cumulative terpolymer composition, we should briefly mention azeotropy. In this case, the ternary reactivity ratios estimated for IS = 0.9 M do not exhibit an azeotrope. However, those estimated for IS = 1.5 M exhibit azeotropic behavior at $f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.26/0.35/0.39. This further emphasizes the customization potential for AMPS/AAm/AAc as we learn more about the solution effects on polymerization kinetics.

3.2.3 Terpolymer Microstructure

Terpolymer microstructure, an important property for customization of materials (as explained in Section 1.2.4), is only discussed as a function of ionic strength herein. Since we have two data

sets where all solution conditions (pH, IS and [M]) are equal (prior work from Scott et al. [5] and Runs #1, #10, #11 from the current study), we can consider terpolymer microstructure at IS = 0.9 M and 1.5 M more consistently.

We are calculating the instantaneous triad fractions for demonstration and in order to get a general understanding about the system. This involves using all possible initial feed compositions ($0 < f_{i,0} < 1$; $\sum_{i=1}^{3} f_{i,0} = 1$) and relevant reactivity ratios to calculate 18 possible triad fractions (recall Equations 3 and 4). As explained previously, 6 triads are centered around each monomer; the full list of triads is shown in Table 7.

Since we are investigating AMPS/AAm/AAc terpolymers for enhanced oil recovery, the material should be acrylamide-rich with an equal distribution of anionic charges, as per references [44, 52]. Therefore, given the triad fractions shown in Table 7, the goal is to minimize "blocky" homopolymer sections (highlighted in red) and to simultaneously maximize alternating behaviour for acidic (charged) comonomers. For the analysis, we assume that AMPS and AAc are both fully dissociated (which is true for any pH > 5), so they both contribute to the desired charge density. Therefore, any triad fraction for which AMPS or AAc alternates with AAm is desirable; these fractions (the sum of which is to be maximized) are highlighted in green in Table 7.

TABLE 7: Possible Triad Fractions for the AMPS/AAm/AAc Terpolymer

| AMPS (1)- centered	AAm (2)-centered	AAc (3)-centered
A_{111}	A_{222}	A_{333}
A_{212}	A_{121}	A_{131}
A_{313}	A_{323}	A_{232}
$A_{112+211}$	$A_{221+122}$	$A_{331+133}$
$A_{113+311}$	$A_{223+322}$	$A_{332+233}$
$A_{213+312}$	$A_{123+321}$	$A_{132+231}$

To better visualize the instantaneous triad fractions, we can plot the likelihood of "blocky" sections occurring in the polymer chain as a function of initial feed composition. This is achieved by summing the A_{111}, A_{222} and A_{333} triad fractions at all feed compositions. Since the triad fractions are predicted using reactivity ratios, the same analysis was completed using reactivity ratios estimated from data at IS = 0.9 M and at IS = 1.5 M (recall Table 6). The results for both analyses are presented in Figure 8.

As expected, the most "blocky" behavior is exhibited for homopolymers ($f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 1.0/0.0/0.0, 0.0/1.0/0.0, 0.0/0.0/1.0). The minimum changes somewhat as we shift from IS = 0.9 M to IS = 1.5 M, but the general trends are the same. In this case, our desire to synthesize a

terpolymer and our desire to minimize "blocky" behavior align: the "blocky" behavior decreases

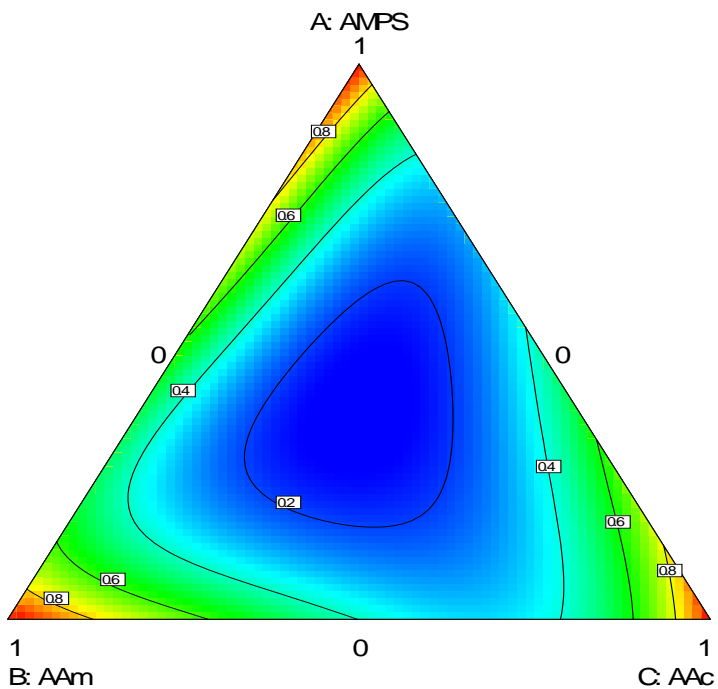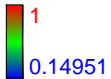as we move towards the center of the composition diagram.

(a)

(b)
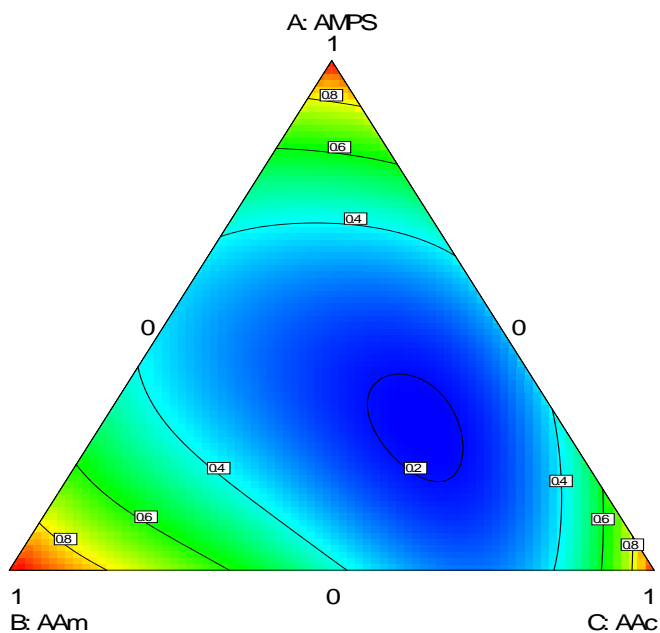
FIGURE 8: Prediction of Instantaneous "Blocky" Triad Fractions at IS = (a) 0.9 M and (b) 1.5 M

Next, we consider the charge distribution along the polymer backbone. Using Design Expert software, we can minimize the "blocky" triad fractions and maximize the desirable triad fractions (that is, those with alternating behaviour of charged comonomers) simultaneously. Additional composition constraints were added (all $f_{i,0} \geq 0.1$) to ensure that the optimized recipes were, in fact, terpolymers. For both IS = 0.9 M and IS = 1.5 M, several solutions exist. Some feed compositions predict fewer "blocky" fractions, others predict more alternating ion behavior. Both requirements are equally weighted for the current study, but more tailoring is possible. The results of both optimizations are presented in Table 8 and Figure 9.

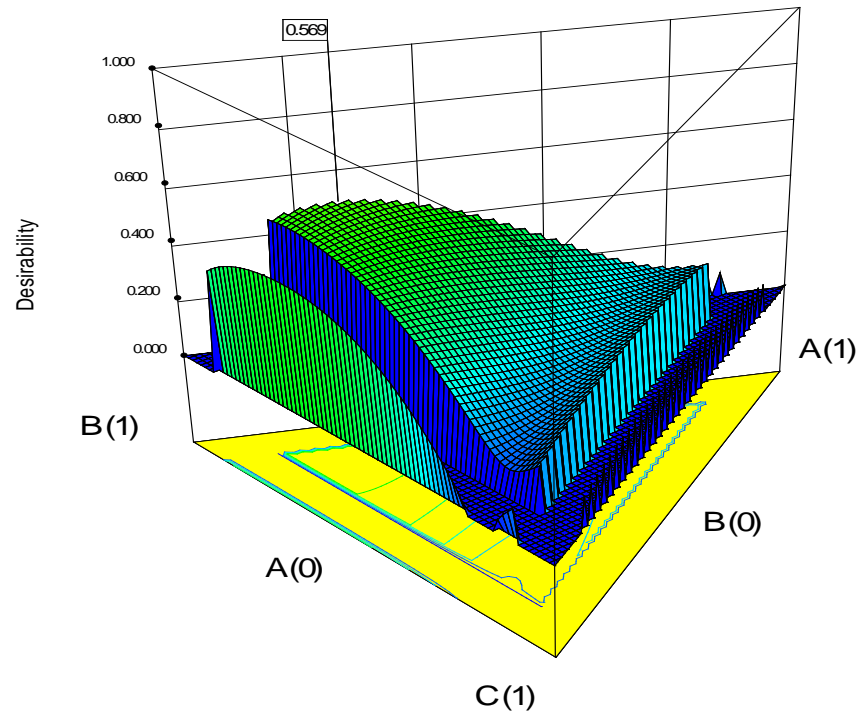**TABLE 8:** Optimized Triad Fractions for Enhanced Oil Recovery

(a) Given Reactivity Ratios Estimated at IS = 0.9 M, pH 7 and [M] = 1.0 M					
Solution #	$f_{AMPS,0}$	$f_{AAm,0}$	$f_{AAc,0}$	"Blocky" (to minimize)	Charge Dist. (to maximize)	Desirability
1	0.209	0.691	0.100	0.487	1.420	0.569
2	0.100	0.750	0.150	0.603	1.508	0.536
3	0.400	0.500	0.100	0.323	1.154	0.490
4	0.500	0.400	0.100	0.305	1.039	0.403
5	0.539	0.100	0.361	0.286	0.890	0.238
6	0.100	0.100	0.800	0.386	0.854	0.159
(b) Given Reactivity Ratios Estimated at IS = 1.5 M, pH 7 and [M] = 1.0 M					
Solution #	$f_{AMPS,0}$	$f_{AAm,0}$	$f_{AAc,0}$	"Blocky" (to minimize)	Charge Dist. (to maximize)	Desirability
1	0.412	0.459	0.129	0.255	1.100	0.521
2	0.400	0.500	0.100	0.301	1.125	0.520
3	0.500	0.400	0.100	0.330	1.121	0.507
4	0.637	0.100	0.263	0.217	0.980	0.448
5	0.100	0.800	0.100	0.521	1.139	0.437

According to the low ionic strength results in Table 8a (IS = 0.9 M, pH 7 and [M] = 1.0 M), the desirability function is maximized for $f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.209/0.691/0.100. This result also aligns with our wish to use an AAm-rich terpolymer; AAm-rich copolymers (with AAc) have been successfully employed for enhanced oil recovery [53]. Alternatively, Solutions 2 and 3 (again from Table 8a) also show promise. The exercise predicts that Solution 2 will have more blocky behavior, but improved charge distribution over Solution 1. In contrast, Solution 3 has less blocky triad fractions, but the negative aspects are the lower AAm content and the poorer charge distribution. Solutions 4 through 6 are not considered further, as the AAm content is likely too low for the EOR application.

The high ionic strength results in Table 8b (IS = 1.5 M, pH 7 and [M] = 1.0 M) show lower desirability values for the top two solutions (compared to the IS = 0.9 M results). In general, the reactivity ratios estimated at higher IS predict less "blocky" triad fractions, but the charge distribution is not as good. This is likely due to the lower acrylamide content, both from a feed composition and an incorporation perspective (as shown in Section 3.2.2). Along the same line, most optimal feed compositions in Table 8b have low $f_{AAm,0}$, which is not ideal for the EOR application. Given the optimized recipes, Solution 5 has the highest (therefore most desirable) AAm fraction, but the overall desirability is lower than for the optimal terpolymerizations at IS = 0.9 M.
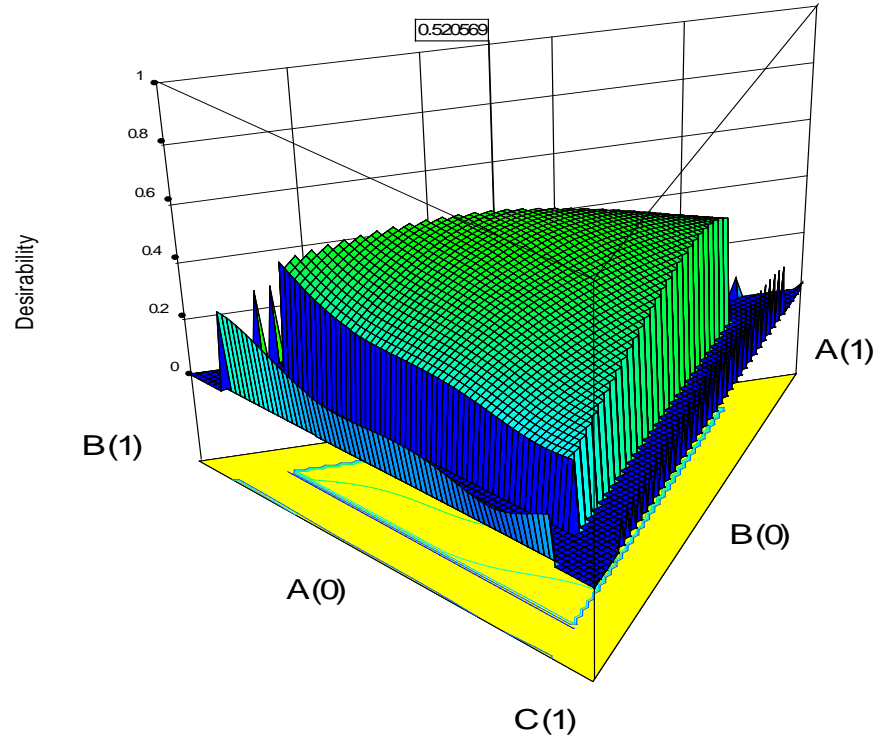
(a)

(b)

FIGURE 9: Optimized Instantaneous Triad Fractions for Enhanced Oil Recovery at (a) IS = 0.9 M and (b) IS = 1.5 M (A = $f_{AMPS,0}$, B = $f_{AAm,0}$, C = $f_{AAc,0}$)

As mentioned earlier, these instantaneous triad fractions were used to demonstrate the basic principles. We now resort to the cumulative terpolymer composition as a function of conversion, given the most desirable feed compositions from Table 8. The most promising optimal recipes are examined for both IS = 0.9 M (Solutions 1, 2 and 3 of Table 8a) and IS = 1.5 M (Solutions 1, 2 and 5 of Table 8b); corresponding cumulative terpolymer composition profiles are shown in Figure 10.

In Figure 10a, all three feed compositions exhibit minimal composition drift. Therefore, along with composition, terpolymer triad fractions should remain relatively constant throughout conversion. As per previous EOR studies by our group (for AAm/AAc copolymers), preference is given to materials with higher acrylamide content [44, 53]. Therefore, Solution 1 or Solution 2 of Table 8a seem the most promising for future EOR testing.

In Figure 10b, the three optimal feed compositions exhibit more composition drift. This is in agreement with our earlier results (recall Figure 6 and Figure 7) but is not a desirable property for this application. Solutions 1 and 2 (from Table 8b) give similar results, but both end up being rich in AMPS. The most viable option at high ionic strength is Solution 5 ($f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.100/0.800/0.100), since AAm is present in the highest proportion. However, as evidenced in Section 3.2.2, the high ionic strength limits AAm incorporation, and therefore the low ionic strength is the better option.
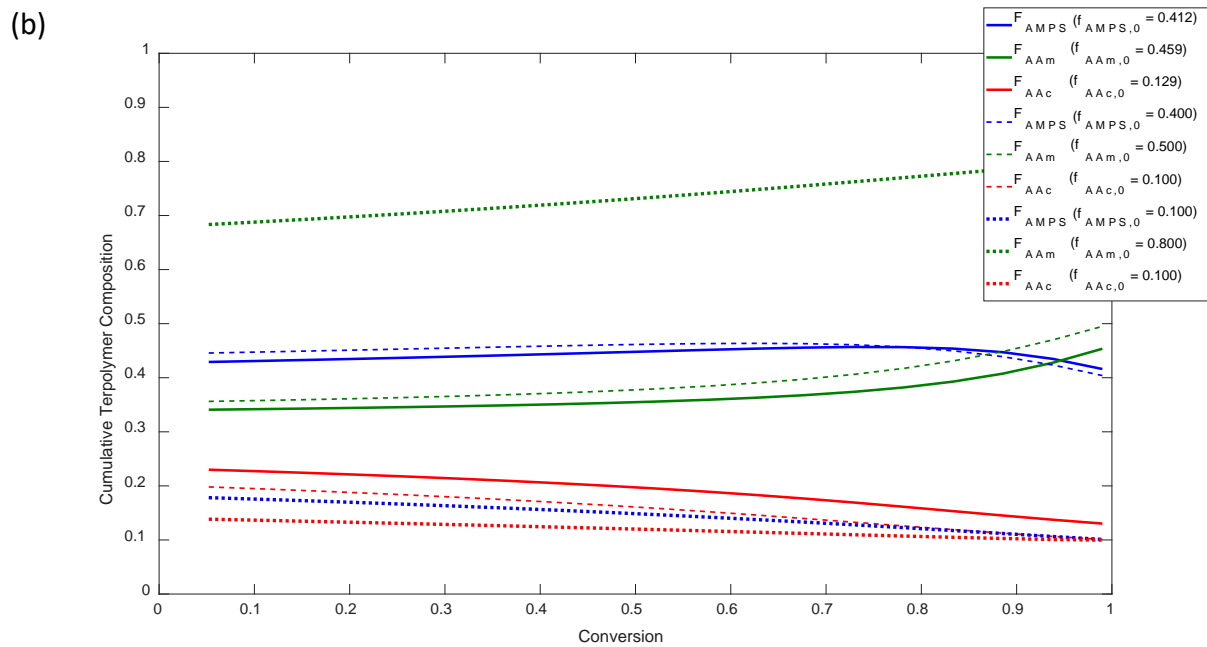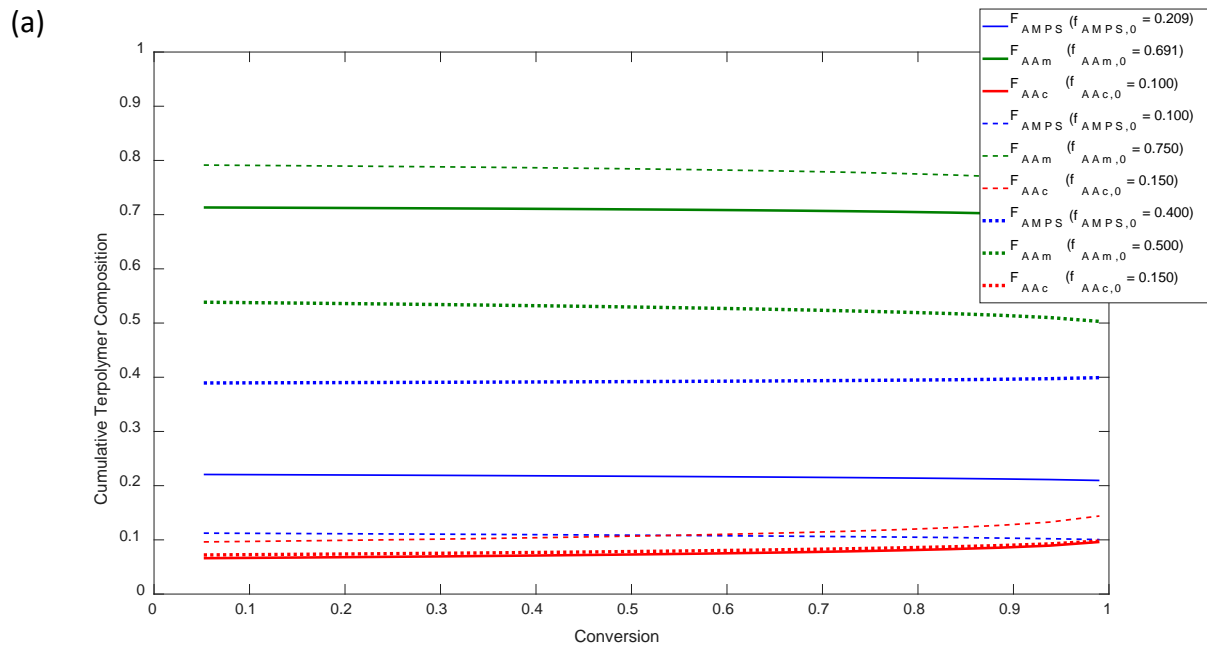
FIGURE 10: Cumulative Terpolymer Composition Predictions from Optimized Triad Fractions at (a) IS = 0.9 M and (b) IS = 1.5 M

Therefore, in future enhanced oil recovery studies, the most promising materials are those synthesized from acrylamide-rich recipes at IS = 0.9 M ($f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.209/0.691/0.100 and 0.100/0.750/0.150). We plan to investigate these further in future EOR testing work.

3.3 Effect of Monomer Concentration

In Section 1.1.3, the effect of monomer concentration on terpolymerization kinetics was discussed. For related copolymer systems, monomer concentration has an impact on reactivity ratios [8]. This is likely due to the change in monomer concentration influencing the ionic strength; higher monomer concentration results in a higher concentration of charged monomers, thereby influencing the ionic strength and associated charge effects described previously.

Again, in this case, we will look at reactivity ratio estimates (for the sake of completeness), as well as properties that we expect will be more affected by [M], namely molecular weight averages.

TABLE 9: [M] Effects on Ternary Reactivity Ratio Estimates for AMPS/AAm/AAc (M_1/M_2/M_3)

[M]	Data from Run #	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
0.5 M	4, 6, 9	1.05	0.65	0.30	1.14	1.81	0.54
1.0 M	1, 2, 7	1.26	0.56	0.27	1.82	2.45	0.50
1.5 M	3, 5, 8	1.06	0.56	0.44	0.94	1.19	0.47

In Table 9 and Figure 11, there are no obvious trends visible; the reactivity ratios do not tend in a particular direction as monomer concentration increases. Many of the reactivity ratio estimates

are similar at different [M] levels (at least for the range and conditions considered), especially the AMPS/AAm comonomer pair (r_{12} and r_{21} estimates). As discussed in Section 3.1, reactivity ratios associated with acrylic acid seem to have more variability. Again, this may be because the incorporation of acidic comonomers (especially AAc) is more affected by changes in the pre-polymerization solution.
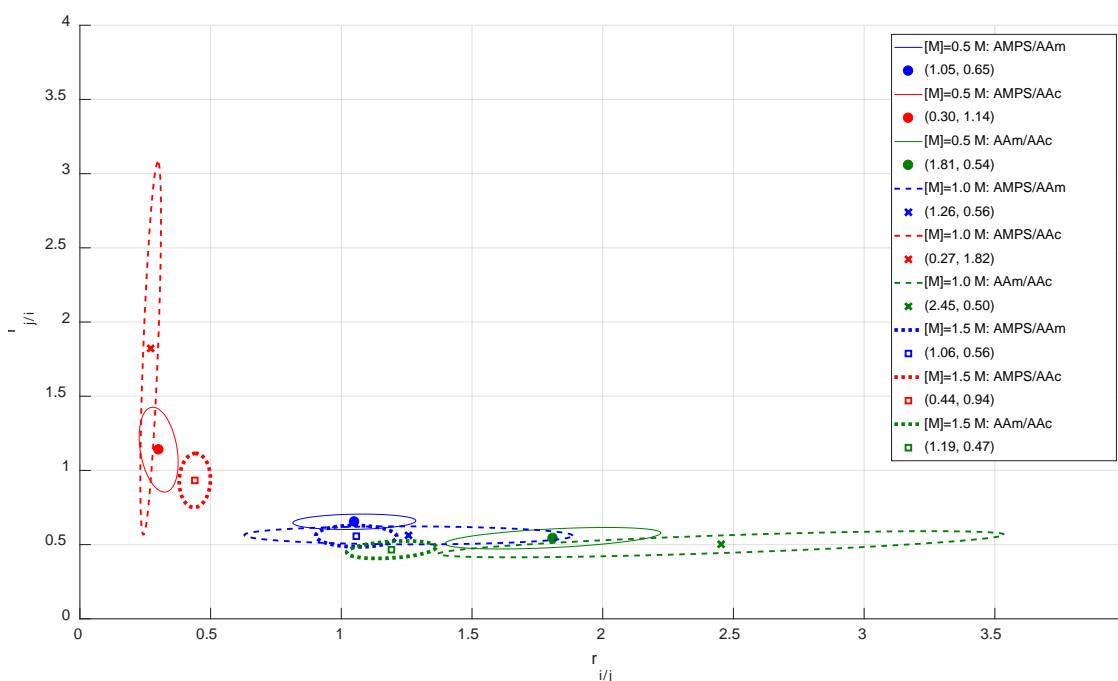

FIGURE 11: Comparison of Reactivity Ratio Estimates for AMPS/AAm/AAc at [M] = 0.5 M, 1.0 M and 1.5 M

As shown in Figure 11, some overlap exists among JCRs for each comonomer pair. In the same way as for the pH effect estimates (Figure 2) and the IS effect estimates (Figure 4), one set of JCRs is much larger than the other two. In this case, the reactivity ratio estimates obtained from data at [M] = 1.0 M show the most uncertainty, especially for r_{12}, r_{31} and r_{23}. Interestingly, the runs used for estimation are Runs #1, #2, and #7 (see Table 9, and refer to Table 2 for detailed

experimental conditions). Therefore, no "common denominator" exists between the three estimations that exhibited higher error. Uncertainty is most likely related to the confounded effects of pH, ionic strength and monomer concentration.

3.3.1 Terpolymer Molecular Weights

Finally, we will examine the peak average molecular weights ($\overline{M}_p$) of all trials. Samples at similar conversion levels (~30%) were selected for analysis, which ensures that any variation in molecular weight is a result of synthesis conditions. Again, the polymer samples are influenced by varying pH, ionic strength and monomer concentration. The results are categorized by feed composition and are presented in Figure 12.
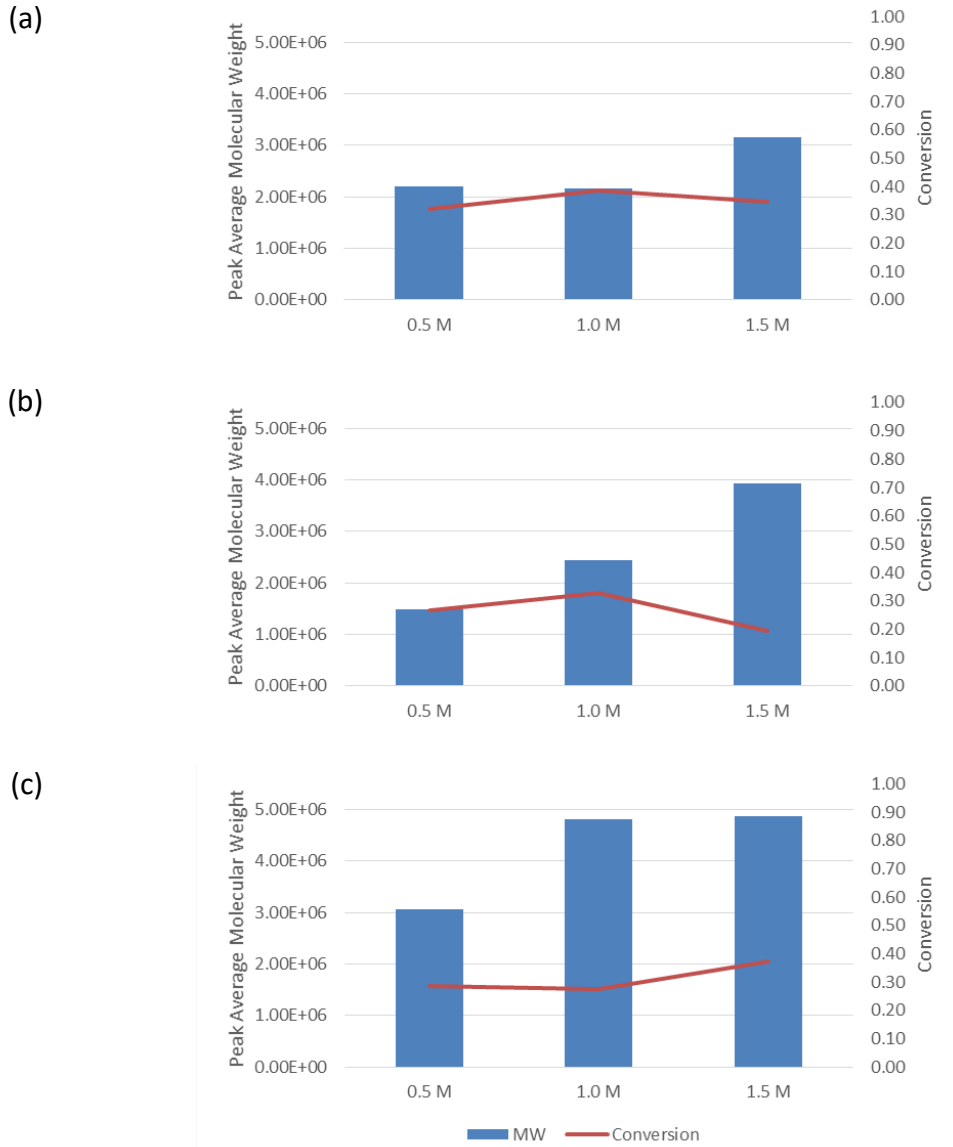
(a)

(b)

(c)

FIGURE 12: Effect of Monomer Composition on Peak Average Molecular Weights for $f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = (a) 0.8/0.1/0.1, (b) 0.1/0.2/0.7 and (c) 0.1/0.8/0.1

As mentioned in Section 2.2, the initiator concentration was adjusted alongside the monomer concentration to ensure that a constant $[M]/[I]^{1/2}$ ratio was maintained. This made it possible to target molecular weight averages that are desirable for enhanced oil recovery (on the order of 10^6 g/mol). There is still a clear increase in $\overline{M}_p$ as $[M]$ increases for all three feed compositions

(Figure 12). The effect of [M] on $\overline{M}_p$ is so significant that it is visible despite other confounding variables; even as pH and IS vary, the trend in Figure 12 is clear.

It is also interesting to observe the effect of feed composition on $\overline{M}_p$. The acrylamide-rich system (Figure 12c) exhibits the highest molecular weight averages of the three optimal terpolymer recipes, at least for the experimental conditions and conversion levels studied. As discussed earlier, high molecular weights are desirable for the enhanced oil recovery application; once again, the acrylamide-rich material is a promising candidate for EOR.

4. CONCLUDING REMARKS

A series of nine terpolymerization experiments (from a definitive screening design) and two complementary experiments (Table 2) has provided us with a wealth of information about the terpolymerization kinetics of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamide (AAm) and acrylic acid (AAc). Solution pH, ionic strength and monomer concentration can all be used to influence the properties of the resulting terpolymer, which ultimately assists with the design of custom materials for enhanced oil recovery and other applications.

Although no clear correlation was observed between pH and reactivity ratio estimates (for $5 \leq$ pH ≤ 9), parameter estimation results suggest that the incorporation of acidic comonomers (AMPS and AAc) is affected by pH. More importantly, comparing these parameter estimates to prior work by Scott et al. [5] revealed cross-over behavior for both AMPS/AAm and AMPS/AAc

comonomer pairs. Since all estimates compared were from experiments at pH 7, other solution effects were explored in more detail.

Ionic strength proved to have the greatest influence on reactivity ratios for the range studied. The two complementary runs confirmed that cross-over behavior exists between IS = 0.9 M and IS = 1.5 M for AMPS-based reactivity ratios (r_{12} and r_{21}; r_{13} and r_{31}) at pH 7 and [M] = 1.0 M. This shift in reactivity ratios has significant potential for tailoring AMPS/AAm/AAc terpolymer properties. With the enhanced oil recovery application in mind, synthesis at the lower ionic strength (0.9 M) is more desirable, as it allows for increased AAm incorporation and a more desirable microstructure. Analysis of terpolymer microstructure suggests that the following feed compositions may be of interest for EOR: $f_{AMPS,0}/f_{AAm,0}/f_{AAc,0}$ = 0.209/0.691/0.100 and 0.100/0.750/0.150.

Finally, monomer concentration had a minor influence on reactivity ratio estimates but had a visible impact on molecular weight averages (even when other factors were varied!). All samples had peak average molecular weights on the order of 10^6 g/mol, but average molecular weights increased with increasing [M] for all feed compositions. This is as expected from theory, but these trends provide good experimental confirmation nonetheless.

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