

## Composition Control Through pH and Ionic Strength During Acrylic Acid/Acrylamide Copolymerization

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**ABSTRACT:** The possibility of controlling the composition of acrylic acid/acrylamide copolymers by controlling the pH and the ionic strength of the reaction medium is investigated. The reactivity ratios of charged monomers depend on the pH of the medium, acrylic acid is the more reactive monomer below pH 3 and acrylamide above pH 4. The working pH was set at 3.6, a candidate for the crossover point, where no composition drift is expected. Copolymerization kinetics is investigated at this pH at various ionic strengths and a reaction without composition drift up to 80% conversion was achieved. All the chains produced in this reaction contain  $30\% \pm 3\%$  acrylic acid. Copolymer conversions, molecular weights, and composition distributions were measured through Automatic Continuous Online Monitoring of Polymerization (ACOMP) system. The copolymerization data were analyzed by a recent error in variables method (EVM) and reactivity ratios are calculated. The results show that in salt free conditions, the reactivity ratios depend on the ionic monomer concentration (ionic strength) in addition to the pH of the reaction medium. The effect of polyelectrolytic interactions on the reactivity ratios and the resulting composition drift during the reaction, sequence length distribution, and Stockmayer bivariate distribution are discussed in detail. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polyelectrolyte; copolymerization; kinetics (polym); reactivity ratio; water-soluble polymer; bivariate distribution

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### INTRODUCTION

Differences in the reactivity ratios result in composition drift during copolymerization reactions. Early production material is richer in the more active monomer than the material produced late in the reaction. When this effect is severe, composition and properties of polymers produced at the beginning of the reaction are very different from those produced late in the reaction. At the end of the reaction homopolymer chains of the less active monomer can be produced.<sup>1</sup>

Microstructure properties are especially important in the coatings and adhesives industry.<sup>2,3</sup> When copolymers with specific properties are desired, product homogeneity is important and composition drift has to be eliminated. Effect of composition drift on the strength of polymer phase boundaries was investigated by Kramer.<sup>4,5</sup>

In research, composition drift is usually avoided by working at a low conversion (less than 5–10%) but this measure is out of question for industry. Composition control can be achieved by controlling the addition rate in emulsion polymerization.<sup>6,7</sup> Various on-line and off line methods and algorithms have been

developed for this purpose.<sup>7,8</sup> Another method is to arrange physical characteristics to compensate for the reactivity ratio differences. For example, using a solvent where the more active monomer is less soluble than the less active one is used to obtain homogenous products.<sup>9</sup>

In polyelectrolyte systems the reactivity ratios may differ widely, the composition drift can be more severe and its undesirable effects more significant. In these systems, the reactivity ratios depend on the pH of the medium and composition control can be achieved by controlling the medium characteristics.

The acrylic acid (Aac)/acrylamide (Aam) system has many fields of applications and new and exciting applications are continually introduced.<sup>10–13</sup> For this reason, this system has been extensively studied.<sup>10–23</sup> The considerable scatter of the published reactivity ratio results is probably due to the effect of various experimental conditions. In the comprehensive study by Wandrey et al.,<sup>22,23</sup> the monomer reactivity ratios were found to be closely correlated with the pH of the medium and  $r_{Aac}$  was seen to decrease and  $r_{Aam}$  to increase monotonically as pH increased from 1.8 to 12, sequential sampling and the basic method of Kelen and Tüdös method were used.

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**Table I.** Reaction Conditions in Acrylic Acid/Acrylamide Copolymerization, Initial and Final pH Values and Dissociation Fractions

Set	Exp. No.	Aac (mol %)	Initial pH	Final pH	Aac (M)	Aam (M)	Diss fract (Aac)	Diss fract (Poly Aac)	NaOH (M)	Total ion conc. (M)	Molecular weight at 80%
1	801	10	3.66	3.71	0.0477	0.423	0.20	0.09	0.0092	0.019	160,000
	620	30	3.61	3.85	0.141	0.329	0.18	0.12	0.0275	0.053	120,000
	614	50	3.69	4.04	0.235	0.235	0.21	0.18	0.0456	0.095	200,000
	616	70	3.63	4.07	0.329	0.141	0.19	0.19	0.0679	0.130	96,000
2	620	30	3.61	3.85	0.141	0.329	0.18	0.12	0.0275	0.053	120,000
	803	50	3.54	3.90	0.141	0.142	0.16	0.14	0.0275	0.050	97,000
	808	70	3.55	3.94	0.141	0.061	0.16	0.15	0.0277	0.051	116,000
3	815	30	3.72	3.81	0.329	0.768	0.22	0.11	0.0680	0.142	260,000
	810	50	3.68	3.98	0.329	0.329	0.21	0.16	0.0680	0.137	206,000
	616	70	3.63	4.07	0.329	0.141	0.19	0.19	0.0679	0.130	96,000

In previous study without added salt, the reactivity ratios were found as  $r_{Aam} = 0.16 \pm 0.04$ ,  $r_{Aac} = 0.88 \pm 0.08$  at pH 2 and as  $r_{Aam} = 1.8 \pm 0.17$ ,  $r_{Aac} = 0.80 \pm 0.07$  at pH 5, respectively.<sup>14</sup> This result suggested that the cross over point, where the reactivity ratios of the two monomers are equal, is expected to be about pH 3.6.

The ionic strength (IS) affects the electrostatic repulsion between the macro radical and the ionic monomer by altering the screening length and it is expected to be a factor in reaction kinetics. There have been suggestions that the IS as well as the pH influences the reactivity ratios.<sup>14,22,23</sup> Losada and Wandrey have shown in their investigation of 1,3-bis(*N, N, N*-trimethylammonium)-2-propylmethacrylate/acryloyloxyethyltrimethylammonium chloride copolymerization, the reactivity ratios obtained at different total ion concentrations, have non-overlapping confidence intervals.<sup>24</sup>

The first aim of this study is to find if the reactivity ratios in Aam/Aac copolymerization also depend on the IS in addition to the pH of the solution. The second purpose is to find the conditions for producing Aac copolymers with no composition drift. In salt free conditions the IS is determined by the concentration of the ionic monomer, in this case Aac. Thus it is impossible to keep both total monomer concentration and IS constant while varying the Aac fraction.

To achieve this purpose, three sets of experiments were performed and the reactivity ratios were calculated for each set. In the first set, following customary practice, total initial monomer concentration was equal in all experiments. Consequently this set was performed at varying IS. The other two sets were performed at low and high constant ISs but varying total monomer concentrations.

The reactions were monitored online by the Automatic Continuous Online Monitoring of Polymerization (ACOMP) system.<sup>1,14,25–28</sup> The data were analyzed by a recent error in variables method (EVM) optimized for obtaining the reactivity ratios by on-line monitoring.<sup>29</sup> The effect of polyelectrolytic interactions on the reactivity ratios are discussed in detail. Composition drift was measured for each experiment, and the impact of composition drift on the chain composition distribution and the Stockmayer bivariate chain composition-molecular weight distribution are discussed.<sup>30</sup>

## EXPERIMENTAL

### Method

In the ACOMP technique, used to monitor the reactions, a small amount of reactor material is continuously removed from the reactor by an isocratic pump and mixed at high pressure with a much larger volume of solvent drawn by another similar pump. The diluted polymer solution is then passed through a light scattering detector (Brookhaven Instruments BIMwA, LS), and an ultraviolet spectrophotometer (Shimadzu SPD-10AV, UV). Data analysis software was written by the authors. The pH of the reactor solution was measured off-line, periodically. The IS was calculated using the Aac concentration, the dissociation fraction calculated from the measured pH value by the Henderson-Hasselbalch equation and the concentration of NaOH used to set the pH.<sup>23</sup>

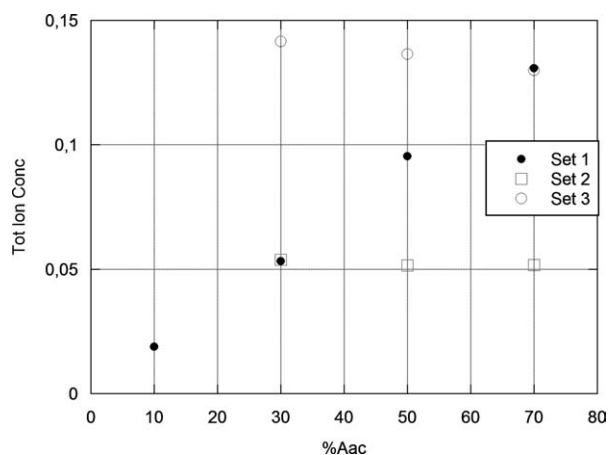
### Polymerization

Aam and Aac were used as received from Aldrich. Water was deionized and filtered by a 0.22  $\mu\text{m}$  filter through a Modulab UF/UV system. The initiator was 4, 4'-Azo bis (4-cyanovaleric acid; ACV, Aldrich) and used as received. Sodium hydroxide (Aldrich) was used to set the pH and 0.1M, NaCl (Aldrich) solution was used as the carrier solvent. Initiator concentration was 8.9 mM and the temperature was 60°C in all experiments. The initiator lifetime at this temperature is  $2.2 \times 10^5$  s,<sup>31</sup> much longer than the time to reach 80% conversion (5000sec). The effect of initiator depletion is neglected.

The monomer, initiator, and NaOH concentrations and the pH values at the beginning and at the end of the reaction are given in Table I for all experiments. Polymerization procedure and determination of comonomer and polymer concentrations from ACOMP follows the procedure in Refs. 14 and 26. Reactions were monitored until increasing viscosity caused the pumps to deprime at 75–85% conversion. Thirty data points were obtained per minute, for clarity only 5% are shown in figures.

## RESULTS AND DISCUSSION

Experimental conditions are given in Table I and summarized in Figure 1. The ionization fractions quoted in the table are calculated from Henderson-Hasselbalch equation, by using literature values,  $pK_a$  (Aac) = 4.26 and  $pK_a$  (poly Aac) = 4.70<sup>23</sup> and



**Figure 1.** Experimental planning: Total ion concentration and Aac fractions of the experiments of Set 1 (filled dots) with constant total initial monomer concentrations but varying IS. In the Sets 2 (open circles) and 3 (open squares) with constant (low and high) IS but varying total initial monomer concentrations.

the measured pH at the beginning and at the end of the experiment. Total ion concentration in Table I column 11 is calculated by adding the dissociated Aac and sodium hydroxide mols.

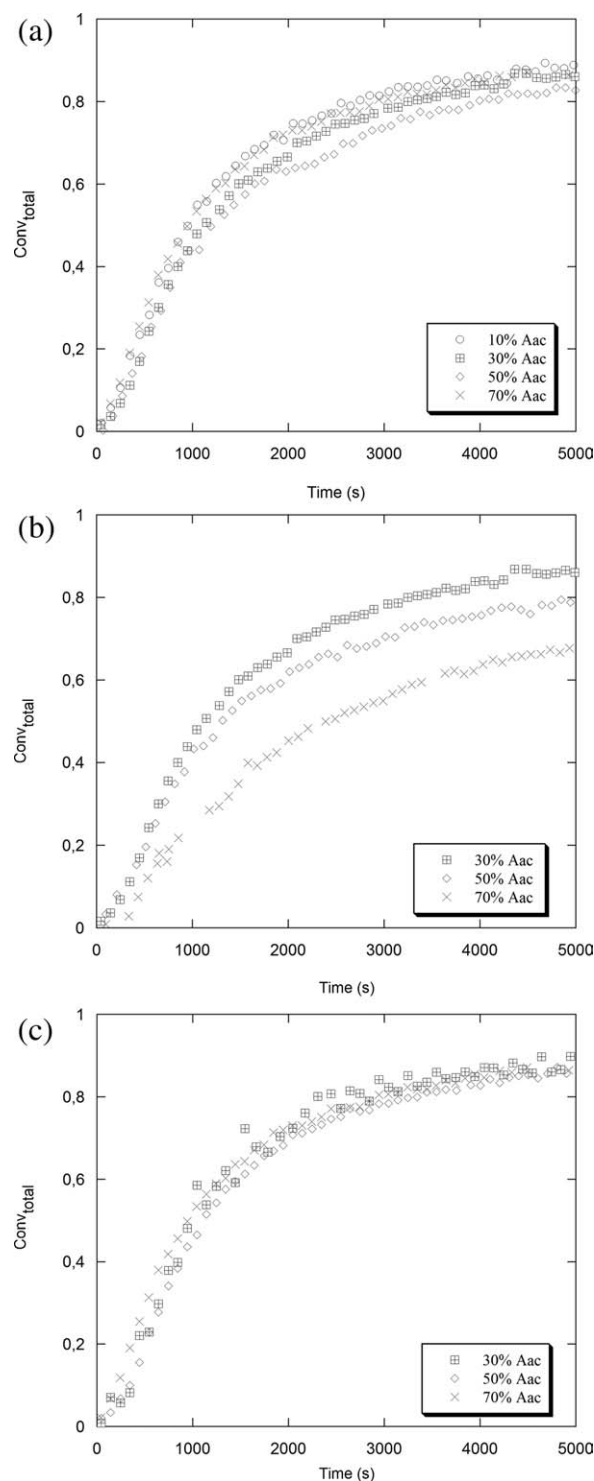
As can be seen from Table I, the pH of the reaction mixture increased slightly with Aac conversion. The increase is more noticeable for experiments with higher Aac content. The difference of the final and initial pH values are 0.05, 0.24, 0.35, and 0.44 for the 10, 30, 50, and 70% Aac experiments of Set 1, respectively. This result is a consequence of the higher  $pK_a$  of the poly acid as compared to the monomeric form.

The conversion time plots for the Set 1 are given in Figure 2(a). In this set of experiments, conducted at constant total initial monomer concentration, the reaction rate is seen to decrease with increasing Aac content from 10% Aac to 50% Aac. The reaction at 70% Aac on the other hand, is as fast as the 10% Aac experiment, the fastest of the group. This non-monotonic behavior may be due to the electrostatic repulsion between charged macroradicals and charged monomers and the suppression of the electrostatic interaction by Debye screening. The conversion time plots for the Set 2 are given in Figure 2(b), which is conducted at constant low ionic strength. This set confirms the trend seen in the Set 1, that is, the reaction rate decreases with increasing Aac fraction. Conversion-time results of Set 3 are given in Figure 2(c). These are conducted at very high IS and shows almost complete independence of the reaction rate from Aac fraction. Here, the screening is so effective that the electrostatic effects on the reaction rate vanish. Except for the experiments conducted at the highest IS, Aam homopolymerization is faster than Aac homopolymerization.<sup>14</sup> This is despite the reactivity ratio of Aac being higher than that of Aam. This behavior may be a result of penultimate effects, which are known to be significant in polyelectrolytes.<sup>32</sup>

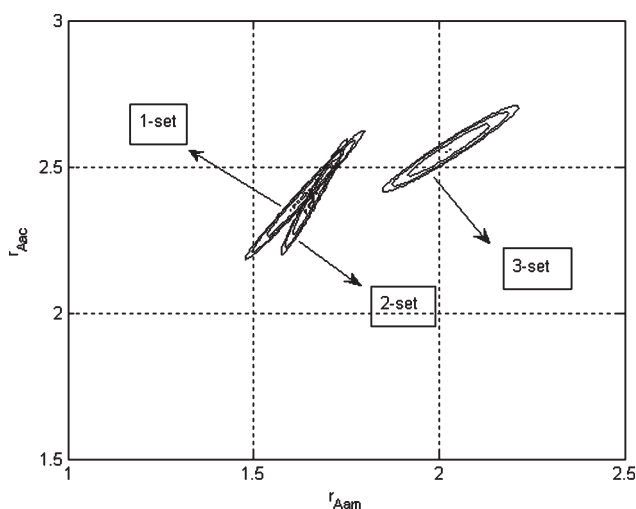
### Reactivity Ratios

The reactivity ratios are calculated by an EVM optimized for on line monitoring.<sup>29</sup> The combined confidence intervals for all

three sets of experiments are shown in Figure 3 and the reactivity ratios are given in Table II. The confidence regions for Sets 2 and 3, conducted at the same pH but different acrylic acid contents (0.141M and 0.329M, respectively) do not overlap. The difference is especially clear in  $r_{Aam}$  values, which are, 1.63 for Set 2 and 1.94 for Set 3. This indicates that the reactivity ratios



**Figure 2.** (a) The conversion time plots for the Set 1. (b) The conversion time plots for the Set 2. (c) The conversion time plots for the Set 3.



**Figure 3.** The combined confidence intervals for the experiments at Sets 1, 2, and 3.

depend on the IS as well as the pH. This dependence is not as strong as the dependence on the pH but is still significant.

Factors which influence the reactivity ratios must be kept constant within the set. Therefore, the reactivity ratios must be determined at constant IS. In salt free conditions, IS, pH and total monomer concentration cannot all be fixed while the fraction of the charged monomer in the feed is varied.

Thus, for salt free conditions, experiment Sets 2 and 3 represent valid protocols, their results being applicable at the experimental pH and IS, but not the experiment Set 1 which is performed at constant total initial monomer concentration but each experiment is performed at a different IS.

### Composition Drift

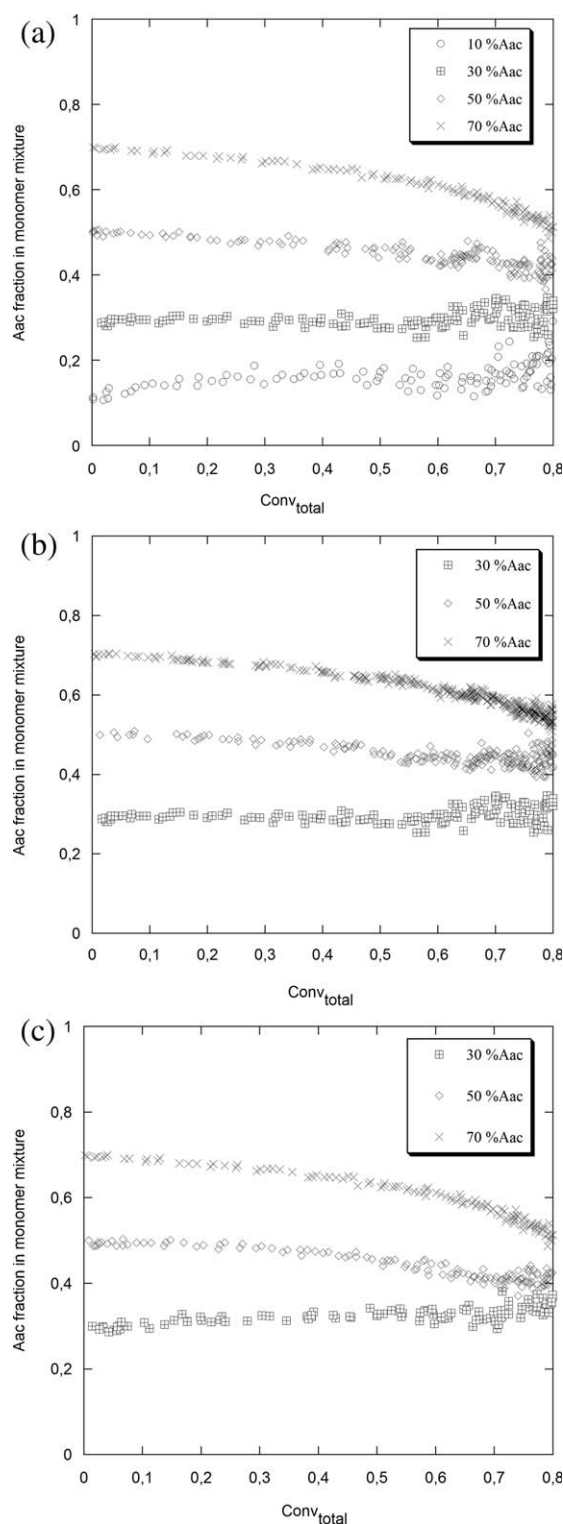
Figure 4(a–c) shows the evolution of the feed composition as a function of conversion for experiments in Sets 1, 2, and 3, respectively. The composition of the polymer produced instantaneously can be obtained from these data through the equation.<sup>26</sup>

$$F_{Aac} = f_{Aac} - (1 - x)(df_{Aac}/dx) \quad (1)$$

Here,  $F_{Aac}$  is the Aac fraction in the instantaneously produced copolymer when the conversion is  $x$  and  $f_{Aac}$  is the Aac fraction in the monomer feed at the same conversion. Note that the scatter in the experimental data increases at higher conversion

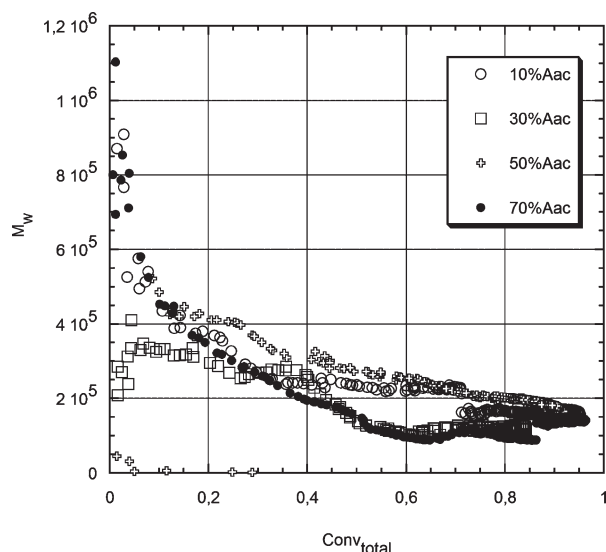
**Table II.** Reactivity Ratios of Acrylic Acid/Acrylamide System at Different pH Values

		$r_{Aac}$	$r_{Aam}$	$r_{Aac}/r_{Aam}$	$r_{Aam}/r_{Aac}$
pH = 2	Ref. 14	0.88	0.16	5.5	0.18
pH = 3.6	Set 1	2.06	1.46	1.41	0.71
pH = 3.6	Set 2	2.35	1.63	1.44	0.70
pH = 3.6	Set 3	2.40	1.94	1.24	0.81
pH = 5	Ref. 14	0.80	1.8	0.42	2.3



**Figure 4.** (a) The evolution of the feed composition as a function of conversion for experiments at Set 1. (b) The evolution of the feed composition as a function of conversion for experiments at Set 2. (c) The evolution of the feed composition as a function of conversion for experiments at Set 3.

because, as both monomer concentrations decrease, relatively small errors in concentration measurements correspond to larger errors in the Aac fraction. Because of this scatter, it is



**Figure 5.** The evolution of molecular weights for the experiments of Set 1.

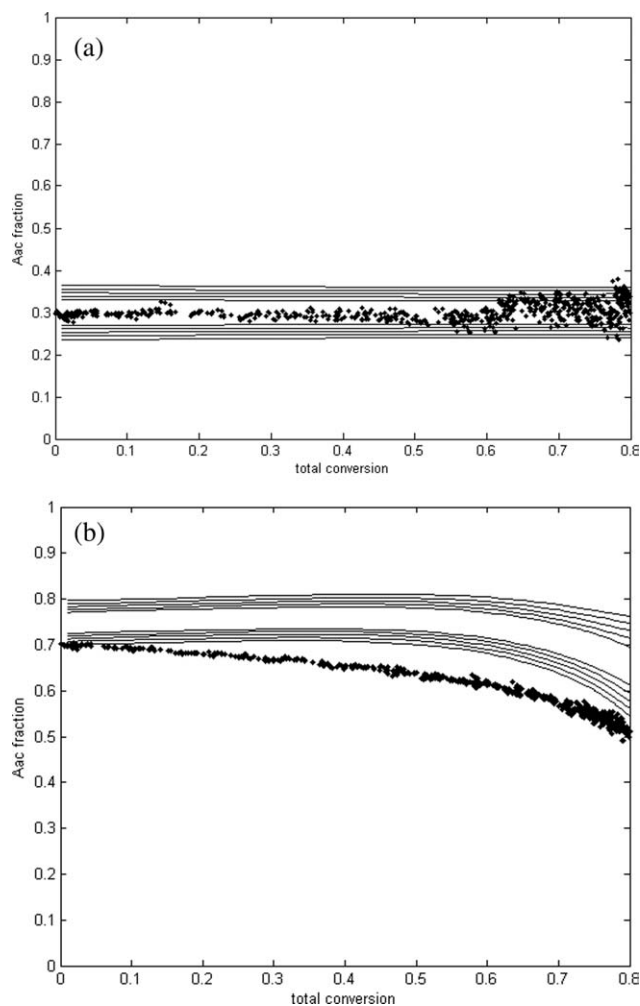
more fruitful to fit for the monomer composition evolution and apply the above formula to the best-fit curve.

Evolutions of molecular weight for the experiments of Set 1 are given in Figure 5. The copolymer composition is then fleshed out using the Stockmayer bivariate distribution with the measured  $M_w$ , and the computed copolymer composition of the incremental polymer produced instantaneously. This is then integrated over molecular weights to find the composition distribution of the instantaneously produced copolymer.<sup>30</sup>

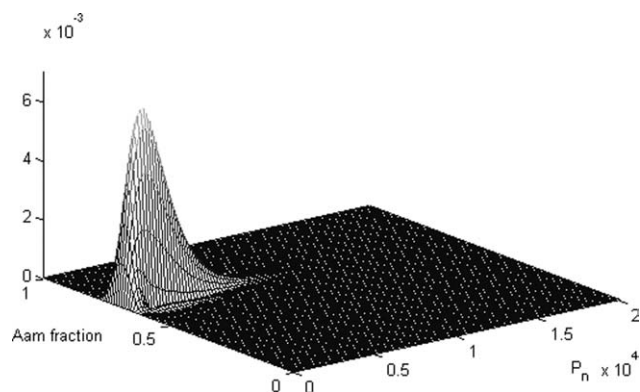
The evolution of the measured monomer composition (dots) and the calculated polymer composition (contours) for the experiment 620 with no composition drift and experiment 616 with moderate composition drift are given in Figure 6(a, b), respectively. In Figure 6(a), the dots representing the monomer composition lie along a horizontal line and the polymer contours are horizontal lines showing that there is no composition drift in this experiment. In experiment 616 with moderate composition drift the copolymer composition begins to change after approximately 60% conversion [Figure 6(b)]. These results may be compared with Figures 4 and 5 in Ref. 14 showing severe composition drift in experiments performed at pH 2 and 5, respectively.

The Stockmayer bivariate distribution of the incremental polymer produced instantaneously is integrated over conversion to obtain the bivariate distribution of the polymer produced throughout the reaction. The result for the Experiment 620 is shown in Figure 7. Figure is symmetric, showing that the lower molecular weight material produced late in the reaction, when the monomer concentrations have decreased has the same composition as the higher molecular weight material produced early in the reaction.

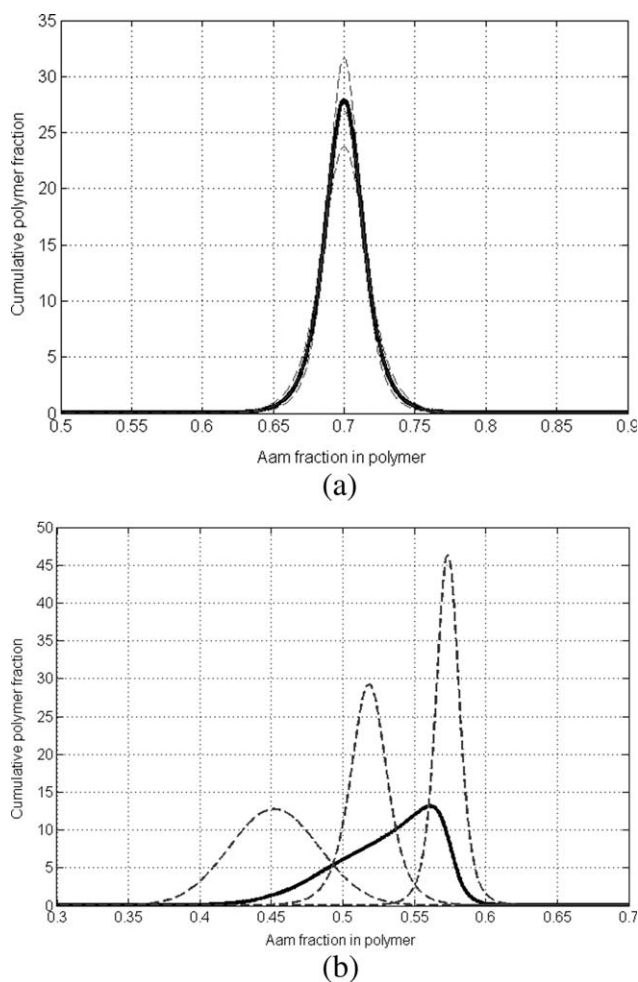
The composition distribution of the overall copolymer is obtained by integrating the overall bivariate distribution over the molecular weight distribution. Experiments 620 with no composition drift and 614 with only a moderate drift are compared in Figure 8(a, b) to see the effect of moderate composition drift on



**Figure 6.** (a) The evolution of the measured monomer composition (dots) and the calculated polymer composition (contours) for the experiment 620 with no composition drift. (b) The evolution of the measured monomer composition (dots) and the calculated polymer composition (contours) for the experiment 616 with moderate composition drift.



**Figure 7.** The Stockmayer bivariate distribution (polymer fraction as a function of the degree of polymerization  $P_n$  and Aam fraction) of the polymer produced throughout the reaction (Experiment 620, without composition drift).



**Figure 8.** (a) The solid line denotes the cumulative composition distribution. The dashed lines show the composition distribution of material polymerized at early in the reaction, at 50% conversion and at the end of the reaction for the experiment 620 (without composition drift). (b) The solid line denotes the cumulative composition distribution. The dashed lines (from right to left) show the composition distribution of material polymerized at early in the reaction, at 50% conversion and at the end of the reaction for the experiment 614 (with moderate composition drift).

the composition distribution of the resulting polymer. Figures show the cumulative distribution (solid lines) as well as the composition distribution of material polymerized early in the reaction, at 50% conversion and at the end of the reaction (dashed lines) for the reactions. The Gaussian distributions for reaction 620 are all centered at 70% Aam. The cumulative curve is also almost Gaussian in shape and shows no broadening. Although reaction 614 has only a moderate composition drift, one can clearly see that the material polymerized early, at mid reaction and late in the reaction have non-overlapping distributions. As a result, the cumulative distribution is broad and asymmetric. The effect of the composition drift is clearly visible.

## CONCLUSION

It was already known that in copolyelectrolyte synthesis the reactivity ratios depend strongly on the pH of the medium.

In this study, it is shown that the reactivity ratios also depend on the IS. As a consequence, the set of experiments for reactivity ratio determinations must be performed under same pH and IS conditions. The recent study of Losada and Wandrey with singly and doubly charged comonomers has also shown the effect of IS on the reactivity ratios.<sup>24</sup>

It is possible to control copolymer composition by choosing appropriate values of pH and IS. It is shown that under right conditions it is possible to produce copolymers with no composition drift throughout the experiment. Achieving a reaction with no composition drift resulted in a copolyelectrolyte of uniform composition by a direct synthesis route without resorting to specialized and difficult techniques.

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