Monitoring the Synthesis and Properties of Copolymeric Polycations

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The kinetics; evolution of molar mass; solution conductivity, \( \sigma \); intrinsic viscosity; and average composition drift; and distribution were determined by monitoring the synthesis of copolymeric polycations of acrylamide (Am) and [2-(acryloyloxy)ethyl]-trimethylammonium chloride (Q9). The quantitative relationship between diminishing \( \sigma \) and charged co-monomers incorporation was monitored for the first time and provided novel data on counterion condensation, which occurs gradually over a broad composition regime. This new capability allows predictions concerning the relationship between copolymer composition and linear charge density, \( \xi \), to be tested and models of trivariate mass, composition, and \( \xi \) distributions to be built. This approach, hence, brings together the previously disparate fields of synthetic chemistry of copolymers and physical chemical properties of polyelectrolytes. Monitoring was achieved with a new implementation of the ACOMP (automatic continuous online monitoring of polymerization reactions) platform. Reactivity ratios determined by ACOMP were \( r_{Q9} = 0.47 \) and \( r_{Am} = 1.10 \). Opposite trends in composition drift and final molar mass were found; low starting percentage of Q9 led to low composition drift and high molar mass, whereas the opposite was found at high starting percentage of Q9. Complementary end-product analysis by multidetector gel permeation chromatography supported the ACOMP results. End-product polyelectrolyte properties were characterized by automatic continuous mixing, revealing that combined electrostatic persistence length and excluded volume effects led to the expected large changes in polyelectrolyte conformation and interactions. These results set the groundwork for semibatch control of molar mass, composition, and \( \xi \), and eventually for monitoring and control for inverse emulsion-based reactions of this type.

Introduction

One of the aims of this work is to establish a link between two separate fields: the chemical synthesis of copolymers and the description of the physical chemistry properties of polyelectrolyte solutions. This is approached here via a new implementation of the ACOMP platform (automatic continuous online monitoring of polymerization reactions), which uses a series of detectors for monitoring the kinetics and evolution of polymer average molar mass, viscosity, and composition distributions, and a conductivity probe to measure solution conductivity changes as charged monomers are incorporated into copolymeric polyelectrolyte chains, here termed “copolyelectrolytes”. The latter data can be combined with the composition data to make deductions about both copolyelectrolyte specific conductivity and the linear charge density, \( \xi \), along the copolyelectrolytes chains, which, due to counterion condensation (CC), does not necessarily follow the composition distribution. Hence, a framework can be developed for modeling the \( \xi \)-distribution and combining it with the other data to have a comprehensive set of average molar mass, intrinsic viscosity, composition, and \( \xi \)-distributions. This new capability should allow predictions about polyelectrolyte end-product character-

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equals $kT$. This work furnishes high-resolution data intrinsically linking co-monomers composition $\xi$ to copolyelectrolytes composition and provides grist for theoretical descriptions. A first, elementary model for obtaining $\xi$ from these data is also proposed herein.

On the synthetic polymer chemistry side, the earliest copolymerization models trace back to the simple “ultimate model” of Mayo and Lewis and have evolved considerably over the decades to include penultimate and other models and definitions of new versions of reactivity ratios to accommodate the models. Actual determination of copolymer composition is a difficult and often tedious task and is the subject of much ongoing research in the polymer characterization community. Cross-fractionation or “hyphenated” approaches are often used, such as calorimetry and densimetry; liquid chromatography; and techniques involving multidetector SEC alone, SEC/NMR, SEC/MALDI, and SEC/thin layer chromatography. Chromatographic techniques for composition analysis were recently reviewed.

ACOMP has recently provided an advance in the area of copolymer characterization by monitoring the evolution of the average composition drift and distribution, in addition to the average molar mass and intrinsic viscosity distributions. The copolymer is, hence, “born characterized”, thus avoiding the difficult end-product determination of the various distributions and also offering the opportunity for control of synthesis reactions.

The test system for this new approach involves acrylamide-based monomers, which find practical application in the major industrial area of synthetic flocculants. Synthetic polymeric flocculants have been widely employed for the past decades in solid—liquid separation processes where colloidal particles fail to settle by themselves. These flocculants promote the recovery or the elimination of the dispersed solids.

Two fundamental characteristics are required of these polymers to accelerate and enhance the efficiency of the procedure: high molecular weight and a certain $\xi$-distribution. The former directly affects particle-bridging, whereas the latter provides charge neutralization, both mechanisms constituting the basis of formation of flocules when a polymeric flocculant is added into a colloidal dispersion. Charge neutralization is usually a feature of polymers of relatively low molecular weight and high $\xi$, whereas bridging is the preferred mechanism for applications of nonionic polymers of more than a million or for high molecular weight polyelectrolytes of low charge density.

Acrylamide is the most extensively used monomer for water treatment, since it polymerizes to form high molecular weight chains. In terms of ionic charge, polyacrylamides are of particular interest because in water, most colloidal particles are usually negatively charged. Acrylamide-based cationic polyelectrolytes fulfill the mass and charge requirements. Such copolymers are expected to be more efficient than either of the respective nonionic or cationic homopolymers. Stable, highly charged, water-soluble, high molecular weight copolymers can be produced in inverse emulsions. The product is a dispersion of fine particles in a solvent, which will readily invert in water so that the water-swollen polymer particles dissolve rapidly. Moreover, the products are stable for long periods and easy to handle.

A thorough understanding of the kinetics and the evolution of polymer properties within the reaction in inverse-microemulsion, however, is still to be established. A long-term objective of this work, hence, is to set the stage for monitoring the synthesis of copolymeric polyelectrolytes (or copolyelectrolytes) in inverse emulsions by first developing the methodology and analyses for homogeneous solution-phase copolymerization. The immediate goals are to (i) monitor kinetics and polymer properties, including $\xi$, during synthesis for a variety of co-monomers starting compositions; (ii) draw conclusions on composition and molar mass drift during the reaction, as well as their relationship to the $\xi$-distribution; (iii) identify end-product polyelectrolyte characteristics, such as ionic strength effects on hydrodynamics and interparticle excluded volume, as a function of co-monomers composition; and (iv) cross-check with a standard GPC method. This work takes advantage of a recently introduced full-spectrum ultraviolet (UV) method in ACOMP for resolving co-monomers of similar spectral characteristics and the combining of conductivity data with the other ACOMP signals. A previous attempt to use a less robust probe led to observation of qualitative trends of $\sigma$, but no quantitative data resulted.

**Materials and Methods**

Acrylamide (99+%, electrophoresis grade; hereafter, Am), potassium persulfate (99+% ACS reagent; hereafter, KPS), [2-(acryloyloxy)ethyl]-trimethylammonium chloride 80 wt % solution in water (inhibited with 800 ppm MEHQ; hereafter, Q9), and ethylenediaminetetraacetic acid tetrasodium salt hydrate 98% (EDTA, chelating agent which suppresses the effect of MEHQ) were purchased from Aldrich and used without further purification. Water was deionized and filtered with a 0.22 μm filter in a Modulab UF/UV system. Q9 and Am are depicted in Scheme 1.

ACOMP background, theory, and instrumentation have been described in detail previously. The ACOMP system in this work used a two-pump, one-stage dilution in a high pressure mixing chamber (HPMC), yielding a 25-fold dilution. The dilution solvent was aqueous 0.1 M NaCl. This moderate ionic strength (IS) medium was chosen to largely, but not completely, suppress the polyelectrolyte properties of the copolymers. A Shimadzu HPLC pump was used for extraction from the reactor, and an Agilent pump was used to bring the solvent to the HPMC. The total detector flow rate was 2.5 mL/min, yielding around 1 mg/mL, depending on the experiment, of combined monomer and polymer concentration in the detector train. Detectors comprised a Brookhaven Instruments Corporation (BI-MwA) seven-angle light-scattering photometer, a Shimadzu differential refractometer (RID-10A), a custom-built single-capillary viscometer, and a Shimadzu photodiode array UV/visible spectrophotometer (SPM-20A). Comonomer concentrations were separated at each instant by the UV method of reference. A thermocouple immersed in the reactor monitored the reaction temperature.

A Jenway 027 213 glass-bodied conductivity probe was immersed in the reactor during reactions and attached to a Jenway 3540 ph/conductivity meter. The probe measured

**SCHEME 1: Monomer Structures**

- Acrylamide
- [2-(acryloyloxy)ethyl]-trimethylammonium chloride

**Table 1: Monomer Structures**

<table>
<thead>
<tr>
<th>Monomer Structure</th>
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<tbody>
<tr>
<td>Acrylamide</td>
</tr>
<tr>
<td>[2-(acryloyloxy)ethyl]-trimethylammonium chloride</td>
</tr>
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**Table 2: Experimental Conditions**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Detail</th>
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<tr>
<td>Monomer</td>
<td>Acrylamide</td>
</tr>
<tr>
<td>Initiator</td>
<td>Potassium persulfate (KPS)</td>
</tr>
<tr>
<td>Initiator Conc.</td>
<td>0.25 M</td>
</tr>
<tr>
<td>Temperature</td>
<td>65°C</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
</tr>
<tr>
<td>Reaction Volume</td>
<td>100 mL</td>
</tr>
<tr>
<td>Water Swell</td>
<td>80%</td>
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<tr>
<td>MEHQ Conc.</td>
<td>800 ppm</td>
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<tr>
<td>EDTA Conc.</td>
<td>98%</td>
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**Table 3: Data Analysis**

<table>
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<tr>
<th>Data Type</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>Measured at 25°C</td>
</tr>
<tr>
<td>Viscometry</td>
<td>Measured at 25°C</td>
</tr>
<tr>
<td>Refractometry</td>
<td>Measured at 25°C</td>
</tr>
<tr>
<td>UV Spectrophotometry</td>
<td>Measured at 25°C</td>
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**Table 4: Results**

<table>
<thead>
<tr>
<th>Result Type</th>
<th>Result Value</th>
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<tbody>
<tr>
<td>Average Molar Mass</td>
<td>2.5 x 10^6 g/mol</td>
</tr>
<tr>
<td>Intrinsic Viscosity</td>
<td>0.1 poise</td>
</tr>
<tr>
<td>Conductivity</td>
<td>10 mS/cm</td>
</tr>
<tr>
<td>Refractometry</td>
<td>0.001</td>
</tr>
<tr>
<td>UV Absorbance</td>
<td>0.5 UV units</td>
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Table 1: Polymerization Experiments Monitored by ACOMP

<table>
<thead>
<tr>
<th>exp no.</th>
<th>Q9 fraction</th>
<th>Q9 concn, [M]</th>
<th>Am, [M]</th>
<th>$M_{w,\text{final}}$, (g/mol)</th>
<th>$[\eta]_{w,\text{final}}$, (cm$^3$/g)</th>
<th>Q9 rate, (s$^{-1}$)</th>
<th>Am rate, (s$^{-1}$)</th>
<th>$R_{G,\text{final}}$, (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0</td>
<td>0.2</td>
<td>600 000</td>
<td>170</td>
<td>0.0005</td>
<td>400</td>
<td>25 mM NaCl Reactor Solvent</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>0.118</td>
<td>0.024</td>
<td>0.176</td>
<td>310</td>
<td>0.0006</td>
<td>0.00067</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>0.152</td>
<td>0.031</td>
<td>0.176</td>
<td>340</td>
<td>0.0006</td>
<td>0.00069</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>0.249</td>
<td>0.050</td>
<td>0.150</td>
<td>286</td>
<td>0.0006</td>
<td>0.00077</td>
<td>470</td>
<td></td>
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<tr>
<td>A5</td>
<td>0.256</td>
<td>0.052</td>
<td>0.151</td>
<td>286</td>
<td>0.0006</td>
<td>0.00078</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>A6</td>
<td>0.381</td>
<td>0.076</td>
<td>0.124</td>
<td>185</td>
<td>0.0007</td>
<td>0.00099</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>A7</td>
<td>0.501</td>
<td>0.096</td>
<td>0.100</td>
<td>137</td>
<td>0.0007</td>
<td>0.001</td>
<td>400</td>
<td></td>
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<tr>
<td>A8</td>
<td>0.614</td>
<td>0.121</td>
<td>0.076</td>
<td>99</td>
<td>0.0008</td>
<td>0.00123</td>
<td>370</td>
<td></td>
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<tr>
<td>A9</td>
<td>0.620</td>
<td>0.124</td>
<td>0.076</td>
<td>110</td>
<td>0.0008</td>
<td>0.00117</td>
<td>420</td>
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<tr>
<td>A10</td>
<td>0.757</td>
<td>0.156</td>
<td>0.050</td>
<td>74</td>
<td>0.001</td>
<td>0.00169</td>
<td>235</td>
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<tr>
<td>A11</td>
<td>0.880</td>
<td>0.176</td>
<td>0.024</td>
<td>22</td>
<td>0.0009</td>
<td>0.0018</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>A12</td>
<td>0.881</td>
<td>0.179</td>
<td>0.024</td>
<td>20</td>
<td>0.001</td>
<td>0.0018</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>A13</td>
<td>0.951</td>
<td>0.194</td>
<td>0.011</td>
<td>2.0</td>
<td>0.0008</td>
<td>0.0019</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>A14</td>
<td>1.000</td>
<td>0.195</td>
<td>1.50</td>
<td>0.0004</td>
<td>100</td>
<td>25 mM NaCl Reactor Solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>0</td>
<td>0.2</td>
<td>4.70 $\times$ 10$^3$</td>
<td>100</td>
<td>0.00079</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>0.23</td>
<td>0.0491</td>
<td>0.1600</td>
<td>123</td>
<td>0.002</td>
<td>0.0017</td>
<td>308</td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>0.54</td>
<td>0.1162</td>
<td>0.1007</td>
<td>110</td>
<td>0.002</td>
<td>0.0024</td>
<td>280</td>
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</tr>
<tr>
<td>B4</td>
<td>0.83</td>
<td>0.1885</td>
<td>0.0400</td>
<td>5.60 $\times$ 10$^3$</td>
<td>0.0022</td>
<td>0.0031</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>B5</td>
<td>1</td>
<td>0.2300</td>
<td>2.00 $\times$ 10$^4$</td>
<td>0.0009</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Conversion of each monomer was over 98% in each experiment. ACM experiments were also carried out on B1–B5.

Conductance in microsiemens. The voltage data were collected by the BI-MwA, where 1 V corresponds to 10 mS. The cell constant factor, $K = 8.99$, allows conductivity, $\sigma$, in mS/cm to be measured from the conductivity probe voltage, $V_{\text{cond}}$ via $\sigma = K \times 10 \times V_{\text{cond}}$. This probe furnished reliable conductance data at medium ionic strength and at the reaction temperatures used.

Before beginning the polymerization reaction, a pure 0.1 M NaCl aqueous solution was pumped through the detector train to obtain the baseline for each instrument. After stabilization, a mixture of Q9 in the desired initial concentration and EDTA (0.083% w/w with respect to overall formulation) in NaCl reactor NaCl molarity was either 0.005 M or 0.025 M; see Table 1) was pumped (0.1 mL/min) from the reactor and continuously diluted with a flow of 2.4 mL/min of NaCl (0.1 M) from the solvent reservoir. The Q9 stabilization step was continuously diluted with a flow of 2.4 mL/min of NaCl (0.1 M with EDTA (0.083% w/w) in a reaction volume of about 180 mL, which was magnetically stirred and continuously purged with nitrogen and kept at a constant reaction temperature ($T = 25$ °C, regardless of the reaction temperature. The reaction vessel contained different initial co-monomers ratios of Am and Q9 for a total monomer concentration of 0.2 M with EDTA (0.083% w/w) in a reaction volume of about 180 mL, which was magnetically stirred and continuously purged with nitrogen and kept at a constant reaction temperature ($T = 60$ °C).

Once the baseline for the reaction solution at 25°C was obtained, the reactor was heated to the desired reaction temperature (60 °C), and a shot of a solution of KPS dissolved in an aliquot of reaction solution (20 mL), previously purged with nitrogen, was added into the reactor to initiate the reaction. Because KPS was used as initiator, the pH was acidic during the polymerization, and imidization does not occur at acidic pH.

Automatic continuous mixing (ACM) was used to compute the second virial coefficient, $A_2$, and to cross-check ACOMP values for $M_w$ and $[\eta]_w$ of the endproducts. The experiments were carried out with a Shimadzu gradient mixer and the same detector train as above. Experiments were run in two different gradient modes: the first ramped copolymer concentration at fixed ionic strength, whereas the second involved a ramp of ionic strength at fixed copolymer concentration to assess the variations of $[\eta]_w$ and $A_2$ with ionic strength.

Multidetector gel permeation chromatography (GPC) was used to determine molar mass distributions of endproducts and as an independent, conventional cross-check on conversion and $M_w$. Endproduct reactor solutions were concentrated by rotary evaporation, dried and redissolved in the GPC eluent and then injected.

The GPC system used LC-ATvp Shimadzu HPLC pump, with Shodex 804HQ and 806HQ columns in series. The injector loop was 100 μL and a flow rate of 0.3 mL/min was used. The detector train included light scattering, RI, viscometer, and UV detection similar to the ACOMP system. Since the polymer samples to be analyzed were polycations, which are notoriously more difficult to analyze by GPC than polyanions, a special GPC eluent was used: (0.2 M NaNO$_2$ + 0.1 M Tris–hydrochloride + 0.02% Na$_3$) at pH 7. The pH = 7 was used only during the GPC analysis, but this was at room temperature and for a short period of time, and no imidization has been reported under these conditions.

Results and Discussion

Table 1 gives a list of batch reactions, the molar fraction of Q9, the conditions, and kinetic and endproduct summary (reaction rate, final ACOMP $M_w$ and $[\eta]_w$). In this work, all concentrations involving composition, including average composition drift and distribution, will be in molar concentration; for example, [Am] (mol/L), whereas in dealing with light-scattering and viscosity, mass concentration will be used; for example, $c_{\text{Am}}$ (g/cm$^3$).

Figure 1 shows combined, typical raw data for a copolymerization reaction (experiment A7 in Table 1), including LS 90°, UV@220 nm, RI, viscosity, and conductivity data. After stabilizing detectors with the 0.1 M NaCl aqueous solvent, Q9 was added at about 1000 s, causing conductance, RI, and UV to increase while the viscosity and light-scattering signals (only raw light-scattering at 90°, LS90, is shown) remain unchanged due to the stream of dilute monomer. At about 2000 s, Am is added, causing a slight decrease in conductance, since the Am
is uncharged and its addition slightly dilutes the reactor contents. UV and RI signals also increase while LS90 and viscosity remain unchanged. At about 2500 s, the temperature of the reactor is raised to 60°C, and the conductance, measured by the sensor inside the reactor, increases. This latter is due to the fact that the viscosity of water falls significantly, from 0.089 cP at 25°C to 0.0467 cP at 60°C. All other signals remain unchanged during the heating period. At 5000 s, KPS was added, and the reaction began. The in situ conductance probe shows a rapid spike due to the KPS addition. The other detectors in the ACOMP train have a time lag of about 300 s from the reactor and, hence, begin to respond to the beginning of the reaction slightly later in Figure 1. As the reaction proceeds, the RI increases slightly, since the \(dn/dc\) of the copolymer is slightly larger than that of each co-monomers and the UV decreases due to the loss of double bonds in both co-monomers. Both light-scattering and viscosity increase as copolymer is formed, whereas conductance drops due to the incorporation of the charged Q9 monomers into less electrophoretically mobile copolymers.

**Comonomer conversion Kinetics, Average Drift and Composition Distributions, and Reactivity Ratios.** To evaluate the conversion of the co-monomers, UV wavelengths from 215 to 270 nm were used in the method described in ref 7. Figure 2 shows the extinction coefficient spectra for Q9 and Am, obtained from the UV raw data. The spectra were determined for both monomers in each reaction, and the values shown are the average values with error bars (one standard deviation from average value). The reproducibility of the spectra is excellent, suggesting that in the future, “library-based” approaches to copolymerization can be used for which it will not always be necessary to determine the spectra in each experiment.

The kinetic data can be fit approximately with first-order curves of the form \(c_A(t) = c_{A,0} \exp(-r_A t)\), where \(r_A\) is the conversion rate for co-monomers A, and the form holds similarly by replacing A with B for co-monomers B and its rate \(r_B\). There is no a priori reason for the decays to be exponential. In fact, rigorously, the only time true first-order co-monomers decays should be found is in the case that \(r_A r_B = 1\), where \(r_A\) and \(r_B\) are the reactivity ratios for co-monomers A and B, respectively. Figure 3 is an example of the co-monomers concentrations vs time for reaction A5, together with first-order fits, which are so close to the data they are difficult to discern. The residuals, nonetheless, shown in the inset, indicate that there is a different structure to the actual co-monomers decays than merely exponential, but the deviations do not surpass even 5% during the first half of conversion, making the exponential decay fit a robust and simple means of characterization.

The continuous stream of concentration data for each co-monomers allows the average composition drift to be followed. The average instantaneous fraction of co-monomers \(j\) in chains formed at any instant of conversion, \(F_{\text{inst},j}\), is given by

\[
F_{\text{inst},j} = \frac{d[m]_j}{d \sum_j [m]_j} \tag{1}
\]

where the sum is over the molar concentration \([m]_j\) of all co-monomers (in this case, two co-monomers).

Figure 4a shows average composition drift for a variety of starting compositions. At low Q9, the drift is very low and becomes increasingly pronounced as the starting amount of Q9 increases. The drift over the major part of conversion is never very large, however, reflecting the fact that the reactivity ratios, while measurably different, are not widely separated. In the computation of \(F_{\text{inst},j}\), first-order fits of the type in Figure 3 were...
first made so that analytical derivatives could be computed in the above equation. Drift values above about $f = 0.95$ become less reliable in the Figure because the derivatives of the first-order fits often diverge more from the data near the end of the reaction.

$F_{\text{inst}}$ allows the average cumulative composition distribution $z(F)$ to be computed by

$$z_j = \frac{df}{dF_{\text{inst},j}}$$

(2)

where $f$ is the fractional total co-monomers conversion and is computed at each instant, $t$, during the polymerization reaction,

$$f(t) = \frac{\sum_j [\text{pm}]/(t)}{[m]_{\text{total},0}}$$

(3)

where $[\text{pm}]_j$ is the molar concentration of co-monomers $j$ in polymeric form and $[m]_{\text{total},0}$ is the total initial molar concentration of co-monomers. Examples of the average distributions are shown in Figure 4b, expressed in terms of $z_{Q9}$.

None of the distributions is especially wide, but it is striking that at low proportions of $Q9$, the distributions are very tall and narrow, that is, of rather uniform composition, whereas increasing the proportion of $Q9$ leads to significantly broader distributions. It is noted that the area under each average distribution curve integrates to be very close to unity in each case.

Since ACOMP monitors the concentration of each co-monomer at every instant, the use of reactivity ratios (RR) for computing these concentrations is obviated. For theoretical and predictive purposes, however, the RR concept remains quite useful. Hence, the ACOMP data are used to compute the RR. These are computed from kinetic data of the type in Figure 3 by a kinetic method that uses the quasi-steady-state approximation in conjunction with the Mayo–Lewis ultimate model. In this, the co-monomer reaction rates, $R_{Q9}$ and $R_{Am}$, are used to determine the reactivity ratios of $Q9$ and $Am$, $r_{Q9}$ and $r_{Am}$, respectively, via

$$\frac{\alpha_{Q9}}{\alpha_{Am}} = \frac{1 + r_{Q9}x}{x + r_{Am}}$$

(4)

where $x = [Q9]/[Am]_0$. Figure 5 shows 1.2% and 2.5% error contours in the computation of the RR, where the best values are $r_{Q9} = 0.47$ and $r_{Am} = 1.10$. The fact that $r_{Q9}$ is less than unity indicates that $Q9$ polymerizes more readily with $Am$ than with itself. This may be due in part to the charge on $Q9$, but also to the bulk of $Q9$’s side group, as compared to $Am$, and the resulting steric hindrance. The inset to Figure 5 shows the data from which the RR were determined.

**Figure 4.** (a) Average composition drift for several experiments: A2, A4, A6, A7, A9, A10, A12. (b) Average composition distributions in terms of $z_{Q9}$ for the same experiments shown in panel a.

**Figure 5.** Error plot for reactivity ratio by the kinetic method. Inner circle is 1.2% error regime; outer circle is 2.5% error regime.

**Conductivity Results and Interpretation.** The in situ conductance probe data were correlated with the consumption of $Q9$ to probe the effects of average linear charge density, $\bar{\xi}$. With the exception of 100% and 25% $Q9$, $\sigma$ vs $[Q9]$ is surprisingly linear, as seen in Figure 6. This also yielded virtually identical values for the first-order rate constant when fitting both $[Q9](t)$ and $\sigma(t)$; that is, in this case, charged co-monomer conversion and $\sigma$ are linearly related. In the simplest model of counterion condensation (CC), the condensation threshold occurs when the linear charge density parameter $\bar{\xi}$ is unity, where $\bar{\xi}$ represents the number of elementary charges per Bjerrum length, $l_B$, which is 0.718 nm in pure water at 25 °C. The contour length of both $Q9$ and $Am$ in a polymer chain is 0.256 nm; hence, CC would occur when $F_{Q9} \sim 0.36$. It is noted, however, that the cationic trimethyl ammonium group is...
approximately 6 Å away from the backbone at the end of a small but flexible chain. Hence, there can be a wide spatial charge-to-charge variation in even adjacent Q9 monomers. With reference to the above phenomenon and depends not only on conductivity vs \([Q9]\). In the most naive case, where CC occurs around the putative threshold value of 0.36 initial fraction of Q9, in chains of \(Q9\) and Am to create a composition drift and, hence, monitor effects on conductivity vs \([Q9]\). Figure 7 shows \(\sigma \partial \phi / \partial [Q9]\) from the linear fits to the conductor vs initial fraction of Q9. In the most naive case, where CC occurs around the putative value of \(F_{Q9}\) close to 0.36, this slope would be a constant below 0.36, then jump to a higher value after 0.36. This is because there will be a greater loss of solution conductivity when a \(Q9^+\) is incorporated into a chain and condenses a \(Cl^-\) along with it. A second mechanism affecting solution conductivity, however, is the chain conductivity itself. This is a fairly complex phenomenon and depends on not only \(\xi\) but also whether the chain is draining or nondraining and the respective friction factors of the Q9 and Am.

The data in Figure 7 show that there is no sharp transition at the putative threshold value of 0.36 initial fraction of Q9. Rather, around this value, there is an increase occurring that is fairly broad and roughly sigmoidal in nature. More powerful approaches to counterion condensation taking into account factors such as chain flexibility and total free energy, counterion entropies, the full nonlinear Poisson–Boltzmann equation, ion correlations, and other effects predict a gradual, rather than sharp, transition and that condensation phenomena are much richer and subject to more factors than the naive theory predicts.

There are two factors leading to the loss of conductivity as Q9 is converted into copolyelectrolyte chains: (i) loss of free Q9 monomer into a chain whose electrophoretic mobility per ionized Q9 is less than free Q9 and (ii) counterion condensation, which, when it occurs, removes both the Q9 cation and the \(Cl^-\) counterion from the total solution conductivity. The total solution conductivity, \(\sigma_t\), can be expressed as

\[
\sigma_t = \sigma_{NaCl} + [Q9]\Sigma_{Q9} + ([Q9]^0_0 - [Q9])(\phi\Sigma_{Cl^-} + \Sigma_{cp})(5)
\]

where \(\sigma_{NaCl}\) is the conductivity due to added salt in the reactor, which is constant during the reaction, \(\phi\) is the fraction of noncondensed \(Cl^-\) counterions, \(\Sigma_{Q9}\) is the specific conductivity (conductivity per mol/L of \(Q9\)) of free Q9 (which includes both the conductivities of the cationic form of the monomer and its \(Cl^-\) counterion), \(\Sigma_{Cl^-}\) is the specific conductivity of \(Cl^-\) and \(\Sigma_{cp}\) is the specific conductivity of the copolyelectrolyte. This is given in terms of conductivity per mole of Q9 enchained. This term does not include the conductivity of the \(Cl^-\) counterion. The latter is contained in the previous term to the left. The two factors that must be experimentally determined are \(\phi\) and \(\Sigma_{cp}\).

We can start with the supposition that to first-order, \(\Sigma_{cp}\) is constant, which implies that there is a significant difference between the conductivity of free Q9 and Q9 enchained in any type of Am/Q9 chain and that there is then a smaller level of effect, depending on the specific mass, composition, and sequence length distribution differences among specific types of chains. With this assumption, the slopes of \(\sigma\) vs \([Q9]\) can be used to compute \(\phi\).

Under this latter assumption that the counterion condensation effect predominates over the changing value of \(\Sigma_{cp}\) in chains of different composition, Figure 8 shows the results for both fractional ionization, \(\phi\), and linear charge density, \(\xi\) (e^-/l_b). To compute this, it was assumed that at low values of Q9, \(\phi = 1\), and that at the highest values, the theoretical limit of \(\phi = 0.36\).
is approached. It was also assumed there was very little composition drift, as seen in Figure 4a. Although the transitions are not as sharp as in the simplest counterion condensation theory, for which the CC is a threshold phenomenon, the actual behavior is not too far off from the overidealized behavior. The main differences are the gradual approach to the full value of \( R(z) \) (the solid curve is only a guide to the eye) and the overestimate of fractional ionization in the naive theory. As mentioned, there are a number of factors that can contribute to these differences, not the least of which is that the naive theory models the polyelectrolyte an infinitely long, thin, uniformly charged rod.

The further significance of these data is discussed below in light of the following conclusions from the evolution of \( M_w \) and \( [\eta]_w \) during synthesis and the ionic strength behavior obtained from ACM.

**Evaluation of \( M_w \) and \( [\eta]_w \).** When the Zimm light scattering treatment is applied to homopolymers, \( M_w \), \( A_2 \), and \( z \)-average mean square radius of gyration \( \langle S^2 \rangle_z \), are obtained immediately by

\[
K' \nu^2 c = \frac{1}{M_w} \left[ 1 + \frac{q^2 \langle S^2 \rangle_z}{3} \right] + 2A_c c + O(c^2) \tag{6}
\]

where \( c \) is the total polymer concentration (g/cm\(^3\)), \( I_R(q,c) \) is the absolute Rayleigh scattering ratio (cm\(^{-1}\)) measured at a given \( q \) and \( c \), and \( q \) is the usual magnitude of the momentum transfer vector given by

\[
q = \frac{4\pi n}{\lambda} \sin(\theta/2) \tag{7}
\]

\( \lambda \) is the vacuum wavelength of the incident light, and \( \theta \) is the angular position of the scattering detector. The approximation applies when \( q^2 \langle S^2 \rangle_z \ll 1 \). \( K' \) is an optical constant, which for vertically polarized incident light is given by

\[
K' = \frac{4\pi^2 n^2}{N_A \lambda^4} \tag{8}
\]

\( \nu \) is the density of the polymer.

The situation is much less straightforward, however, for copolymers, as detailed by Benoit and Bushuk,\(^{54} \) and Stockmayer et al.\(^{55} \) For copolymers, \( \nu \) is the mass-weighted sum of the refractivities of the corresponding homopolymer of each co-monomer constituent and can be measured directly in an auxiliary experiment.

In the case of copolymers, however, the quantity \( K' \nu^2 c/I_R(q,c) \) extrapolated to \( c = 0 \), and to \( q = 0 \) yields only an apparent molecular weight, \( M_{ap} \): \n
\[
\frac{1}{M_{ap}} = \lim_{q \to 0} \frac{1}{c \to 0} K' \nu^2 c / I_R(q,c) \tag{9}
\]

Enohyaket et al.\(^{56} \) recently demonstrated that the true \( M_w \) can be obtained from continuous measurements of \( M_{ap} \) and the concentrations of each co-monomer, for an arbitrary number of co-monomers, \( N \), according to

\[
M_w(f) = \frac{1}{f} \int \frac{d \left[ f' M_{ap} (f') (\sum_j y_j (f') \nu_j)^2 \right]}{\left( \sum_j E_j (f') \nu_j \right)^2} \tag{10}
\]

where \( y_j(t) \) is the cumulative mass fraction of co-monomer \( j \) at time \( t \), given by

\[
\gamma_j(t) = \frac{c_j(t)}{\sum_j c_j(t)} \tag{11}
\]

The relationship between \( M_w \) and \( M_{ap} \) is highly dependent on the details of the copolymer and the values of \( \nu \), \( M_{ap} = M_w \) only if \( \nu_1 = \nu_2 \) or if there is no composition drift at all (i.e., \( r_1 = r_2 \)). When composition drift is low (i.e., \( E_j \) varies little during conversion) then \( M_{ap} \approx M_w \), and this also holds if \( (\nu_1 - \nu_2)/\nu \ll 1 \). This latter condition holds in this work, because this quantity remains around 0.2 in all the reactions.

Carrying out the calculation converting \( M_{ap}(f) \) to \( M_w(f) \) using the above integral leads to corrections no higher than 4% in any of the data sets. Hence, the homopolymer approximation is excellent and can be used also to compute \( \langle S^2 \rangle_z \) and \( A_2 \).

The endproducts of several reactions were analyzed by GPC as described above. The results for \( M_w \) obtained were in excellent agreement with the ACOMP values. Polydispersities were typical of free radical reactions, but broader for most cases, with \( M_w/M_n \approx 2 \) and \( M_w/M_n \approx 3 \).

Figure 9a shows \( M_w \)-vs-\( f \) analysis for different experiments. The decrease in \( M_w \)-vs-\( f \) is typical of free-radical polymerization in the quasi-steady state approximation where the lifetime of
the initiator is long as compared to the total time of conversion and chain transfer processes are negligible. The trend is that the higher the starting percentage of Q9, the smaller $M_w$ throughout the reaction, including in the final product. The effect is quite dramatic, and the spread of final values of $M_w$ is over a factor of 40.

It is recalled that $M_w$ measured by ACOMP is the cumulative value of this quantity in the reactor at any instant. The instantaneous value, $M_{w,inst}$, can be computed from this by $^{57}$

$$M_{w,inst}(t) = \frac{d(M_w)}{dt}$$  \hspace{1cm} (12)

An example of this computation is shown for experiment A2 in the inset of Figure 9a. The trend of $M_{w,inst}(t)$ is similar to $M_w$.

The weight-averaged reduced viscosity $\eta_{r,w}$ was computed from the data at each instant, without any calibration factor, according to

$$\eta_{r,w}(t) = \frac{V(t) - V(0)}{V(0)c(t)}$$  \hspace{1cm} (13)

where $V(0)$ is the viscometer voltage when pure solvent flows, and $c(t)$ is the total copolymer concentration. The intrinsic viscosity $[\eta]$ is related to $\eta_r$ according to

$$[\eta] = [\eta] + \kappa H_2 [\eta]^2 c_p + \kappa H_2 c_p^2 + O(c_p^3)$$  \hspace{1cm} (14)

where $\kappa H_1$ is $\sim 0.4$ for neutral polymers. $^{58}$ ACM experiments (below) with polymer concentration gradients showed very little

dependence of $[\eta]_{w,final}$ first rises, quickly reaches a maximum, then decreases monotonically. This is related to the electrostatic stiffening of the polyelectrolyte coils as $\xi$ increases, leading to higher viscosity, whereas such effects are absent for pure Pam ($\xi = 0$), and relatively small for very low values of $\xi$.

It is pointed out that earlier reports have been made on the relationship between $[\eta]_{w}$ and $M_w$ for polycations consisting of copolymers of acrylamide and quaternary ammonium acrylic co-monomers. $^{59,60}$ Empirical laws were established for $[\eta]_{w}$ vs $M_w$ in ref 25 at high ionic strength, 1 M, whereas ionic strength dependence of $[\eta]_{w}$ was empirically established in ref 24. The $M_w$ ranges in these works were $> 10^6$ so that direct comparisons with this work ($M_w$ from $1.5 \times 10^4$ to $6 \times 10^5$) are not possible.

Defining the drift in $M_w$ as $\Delta M_w/M_{w,final} \equiv [M_w(f = 0.2) - M_w(f = 1)]/M_w(f = 1)$ yields a roughly parabolic trajectory as the initial fraction of Q9 varies from 0 to 1, as shown in Figure 10b, with a maximum value of 1.5 at about 0.6. The reason for the $M_w$-vs-$f$ slope is steep at very low $f$. For free radical homopolymerization in the quasi steady state approximation (QSSA) where chain transfer processes are negligible and the initiator lifetime is long as compared to the time for total conversion to occur, $M_w(f)$ is given by

$$M_w = M_w(f = 0)\left(1 - \frac{f}{2}\right)$$  \hspace{1cm} (15)

Hence, for the ideal QSSA case, $\Delta M_w/M_{w,final} = 0.8$. The case of pure Am gives very close to this value ($\Delta M_w/M_{w,final} = 0.85$), whereas comparable initial amounts of Am and Q9 yield an increasing $\Delta M_w/M_{w,final}$, which then descends from its maximum of 1.5 to 1.05 for pure Q9. Naturally, the higher values of $\Delta M_w/M_{w,final}$ lead to greater polydispersity.

Taken together, the quantitative information on composition, $M_w$, and $[\eta]_{w}$ drift should allow the design of semibatch experiments in which one or more monomers are flowed into the reactor in a programmable fashion (i.e., not necessarily at a constant rate) to achieve the type of average mass and composition distributions desired. This forms the basis of ongoing work.

Relevant precedents for semibatch inverse-emulsion-based synthesis of acrylamide and quaternary ammonium co-monomers have been provided by Hunkeler et al. $^{61,62}$ and a general approach to semibatch has been extensively discussed by Hamielec and MacGregor. $^{63}$ A recent work provides models for programmed reactant feed policies for maintaining constant composition during free radical copolymerization. $^{64}$
TABLE 2: ACM Results for the Polymer Ramps at 100 mM NaCl from End Products of Experiments B1–B5

<table>
<thead>
<tr>
<th>% Q9</th>
<th>Mw g/mol</th>
<th>A2 mol-cm3/g2</th>
<th>[η]eq cm2/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>151,820</td>
<td>5.4440 × 10⁻⁴</td>
<td>59.41</td>
</tr>
<tr>
<td>21</td>
<td>131,720</td>
<td>1.6018 × 10⁻³</td>
<td>28.478</td>
</tr>
<tr>
<td>52</td>
<td>111,020</td>
<td>2.0114 × 10⁻³</td>
<td>36.46</td>
</tr>
<tr>
<td>82</td>
<td>39,900</td>
<td>2.7986 × 10⁻³</td>
<td>0.375</td>
</tr>
<tr>
<td>100</td>
<td>13,325</td>
<td>6.8435 × 10⁻³</td>
<td>8.485</td>
</tr>
</tbody>
</table>

* dc/dc = 0.176 for all samples.

**ACM Results.** Table 2 gives ACM results for experiments B1–B5 in Table 1. In these experiments, the polymer concentration was ramped continuously from zero to 0.003 g/cm³ in 100 mM NaCl aqueous solvent. A2 increases as percent Q9 increases due to two effects: First, even neutral polymers in a good solvent show a power law of the form A2 ∝ M⁻⁰·₂ so that there is a slight decrease in A2 as M increases. Second, fitting Table 2 data for A2 vs Mw with a power law yields A2 ∝ M⁻⁰·₅. This is, the much larger dropoff with mass is also related to the decrease in linear charge density, E.

The effective viscometric radius, Rp, can be found from viscosity measurements for illustrative purposes by starting with the Flory equation for the intrinsic viscosity of polymer chains in the nondraining limit in the absence of excluded volume effects, [η]0; that is, applicable to polymers in theta solvents.

\[ [\eta]_0 = 6^{\frac{3}{2}} \Phi M \langle S^2 \rangle_0^{\frac{3}{2}} \]  

where \( \Phi = 2.56 \times 10^{23} \) mol⁻¹. Flory and Fox⁶⁵ proposed using eq 16 with the measured, good solvent value [η]0 and, hence, the perturbed values of \( \langle S^2 \rangle_0 \); that is, \( \langle S^2 \rangle \). They introduced the viscosity expansion factor, αp, relating the good solvent to theta solvent viscosities via [η] = αp[η]0. Extensive work on deriving expressions for αp has been carried out over the years.²³,⁶⁶ For the purposes at hand, we define the effective viscometric radius according to the experimentally measured values of [η]w and Mw by

\[ [\eta]_w = 6^{\frac{3}{2}} \frac{\Phi}{M} R_p^3 \]  

Next, the equivalent excluded volume radius, R_eq, can be obtained from the ACM A2 data by

\[ A_2 = \frac{N_A 32 \pi R_{eq}^3}{2 M^2} \]  

The two types of radii, Rp and R_eq, allow the effect of Q9 on copolyelectrolyte coil flexibility and excluded volume to be conveniently assessed via the notion of the apparent persistence length, Lp.²⁵ The wormlike chain expression for a polymer chain with no excluded volume is⁶⁸

\[ \langle S^2 \rangle_0 = \frac{L_p^2}{3} - L_p^2 + 2L_p^3/L - 2 \left( \frac{L_p^4}{L^2} \right) \left[ 1 - \exp(-L/L_p) \right] \]  

where L is the contour length of the polymer, Lp is the persistence length, and \( \langle S^2 \rangle_0 \) is the polymer coil’s unperturbed mean square radius of gyration. The measured \( \langle S^2 \rangle \) for a polyelectrolyte in a good solvent is larger than \( \langle S^2 \rangle_0 \) due to electrostatic excluded volume effects, but these effects cannot be distinguished from local stiﬃng effects experimentally.

The two characteristics are often related to each other by the static expansion factor, αp, by \( \langle S^2 \rangle = \alpha_p^2 \langle S^2 \rangle_0 \). Hence, in earlier works, \( \langle S^2 \rangle_0 \) was replaced by \( \langle S^2 \rangle \), and the resulting persistence length obtained from equation 18 was termed the “apparent persistence length”, Lp, which is a nearly mass-independent measure of polyelectrolyte coil “expansivity”, which is related to the true persistence length in the coil limit by Lp = αp²Lp. The Lp approach allows comparing chains of different M, since the effect of chain length is reduced through the consolidation of electrostatic stiffening and excluded volume into the single parameter, Lp. In this sense, it is an “apparent stiffness” because it also includes chain expansion due to long-range excluded volume effects in addition to local chain stiffening, which is the only effect described by true persistence length Lp. Lp is robust in this sense, since it varies weakly with M, at a maximum as M⁰·₂. This latter assertion is a consequence of the experimental and theoretical limits of the scaling coefficient β in \( \langle S^2 \rangle^{1/2} = b M \beta \), falling in the range of 0.583–0.600.

Analyses based on the combination of electrostatic persistence length (EPL) and electrostatic excluded volume (EEV) approaches⁶⁹–⁷¹ have allowed the separate EPL and EEV components of Lp to be computed without use of any adjustable parameters, and this has led to good agreement with experimental²² and Monte Carlo results. Such calculations are not pursued here.

Figure 11 shows Lp computed by substituting in place of \( \langle S^2 \rangle_0^{1/2} \) in equation 19 (i) the Rp from [η]w and (ii) R_eq from A2, according to eqs 17 and 18, respectively. These values for Lp can be termed Lp,η and Lp,eq. The value for pure Pam of Lp,eq ≈ 8 Å is very typical of a highly flexible, neutral polymer. The fact that both Lp,η and Lp,eq increase with increasing percent of Q9 shows the increasing electrostatic effects of the more highly charged chains, even at the moderate ionic strength of 0.1 M where the measurements were made.

What is also interesting is that Lp,eq increases considerably more than Lp,η, and this is related to the inherent difference in hydrodynamic volume (from [η]) and total excluded volume (from A2). The expansion of the polyelectrolyte coil due to EPL and EEV leads to an increase of hydrodynamic volume, reflected in the increased intrinsic viscosity as the percentage of charged monomer (Q9) increases. The fact that Lp,eq from A2 is significantly greater is rooted in the additional “soft” interaction of electrostatic excluded volume. Whereas increasing coil size...
uncharged polymer, as expected for fluidic-like behavior in non-free-draining conditions. However, for charged copolyelectrolytes, the conformation is more weakly dependent on the number of monomers, \( N \), as the hydrodynamic volume is proportional to hydrodynamic volume and, hence, sensitive to the number of monomers. The effect of increasing ionic strength on the intrinsic viscosity of two copolyelectrolytes of different composition is seen using ACM where polymer concentration is held fixed and ionic strength ([NaCl], mol/L) is continuously varied. In contrast, the homopolymer of Am is unaffected by [NaCl]; B1, B2, B3. (b). A2 vs [NaCl] (M) for several copolyelectrolytes and Pam; B1, B2, B3, and B5.

A further effect in considering polyelectrolyte hydrodynamic size is where the coil falls in the limits of free-draining and non-draining. In free-draining, \( \eta \) is completely independent of \( M_w \) and \( \phi \), as there is relatively little composition drift in the various reactions and, most importantly, no reaction drifts over the range of strongly changing \( d[Q9] \), which occurs for starting \( [Q9] \) fractions between 0.3 and 0.6.

On the other hand, since \( d\Sigma_{cp}/d[Q9] = 0 \), this can be written as

\[
\frac{d\Sigma_{cp}}{d[Q9]} = \frac{d\Sigma_{cp}}{dM_w} \frac{dM_w}{d[Q9]} = 0
\]

and, since \( (dM_w/d[Q9]) \neq 0 \), as amply seen in Figures 9a and 10b, which show large drifts in \( M_w \) during synthesis, we are left with the interesting conclusion that

\[
\frac{d\Sigma_{cp}}{dM_w} = 0
\]
and hence different $\mathrm{d}\sigma/\mathrm{d}[Q9]$ these $M_w$ drifts span, it is clear that $\mathrm{d}\sigma/\mathrm{d}[Q9]$ should be far from constant in a given reaction if $\mathrm{d}2\sigma/\mathrm{d}M_w = 0$.

Although there are a number of ways the independence of electrophoretic mobility on polymer molecular weight can be rationalized from the results here, it will suffice to note that this phenomenon was predicted theoretically by Hermans and Fujita, and demonstrated experimentally by Hoagland et al. over a very wide range of molecular weights and solution ionic strength conditions.

Conclusions

A new ACOMP platform and analysis procedure were developed for quantifying the many aspects of the synthesis of copolymeric polyelectrolytes and drawing together aspects central to synthetic polymer chemistry (average composition drift and average composition, molar mass, and intrinsic viscosity distributions) with the physical chemistry characteristics of solution conductivity and copolyelectrolyte linear charge density $\xi$. In this case, the data indicate that $\xi$ follows the composition distribution directly. The data likewise predict that in cases of high composition drift, the counterion condensation composition region could be traversed during synthesis, leading to a $\xi$ distribution that does not linearly track the composition distribution.

In the case studied here, co-monomers had similar spectra but very different physical properties; that is, in this case, Q9 is cationic and Am is electrically neutral. A recent full spectrum UV addition to ACOMP analysis allowed separation of the co-monomers despite only small spectral differences. An anticorrelation of composition drift and final $M_w$ was found, in which the former was largest at high initial [Q9] and the latter largest at low initial Q9. Drift in $M_w$, expressed as $\Delta M_w/M_{w,\text{final}}$ was maximal when starting Q9 and Am molar amounts were comparable.

Novel evidence for counterion condensation is found in the slopes of conductivity vs [Q9] during each reaction. The higher slopes at higher [Q9], above the putative counterion condensation threshold, are presumably due to much larger losses in solution conductivity when a free cationic monomer is enchain in a growing polymer along with a condensed counterion, as opposed to when the counterion remains free upon monomer incorporation into the chain. The condensation occurs over a broad range of compositions, as expected in all but the simplest of models. Future work will explore predictions of nonlinear conductivity vs consumption of charged co-monomers in systems of co-monomers with widely different reactivity ratios.

Strong polyelectrolyte behavior as a function of both $\xi$ and ionic strength was found in $A_2$ and $[\eta]_m$, and rationalized for both ACOMP and ACM results in terms of combined electrostatic persistence length and electrostatic excluded volume effects.

The intriguing constancy of $\mathrm{d}\sigma/\mathrm{d}[Q9]$ found in any given reaction is traced both to low composition drift and the deduction that $\mathrm{d}2\sigma/\mathrm{d}M_w = 0$. The most probable explanation for this latter finding is found in the nondraining limit of the polyelectrolyte when $kR \gg 1$. It is noted that in future work, deviations from linearity of $\mathrm{d}\sigma/\mathrm{d}[\text{charged monomer}]$ may also be found for copolyelectrolytes not in the nondraining limit or not in the limit of $kR \gg 1$.

This work prepares the way for the next two steps: (1) Use of semibatch operation (that is, controlled reagent feeds) to vary kinetics, composition drift, and $M_w$ distributions and (2) adaptation of the ACOMP monitoring approach to copolyelectrolyte synthesis in inverse emulsions. The monitoring of the synthesis of homopolymeric Am in inverse emulsions was recently demonstrated. Finally, when (1) and (2) are accomplished, it will then become possible to produce tailored copolyelectrolytes “on-command”, aided by feedback-controlled ACOMP.

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References and Notes

(3) Odijk, T. Biopolymers 1979, 18, 3111.
(19) Wilson, R. W.; Bloomfeld, V. A. Biochemistry 1979, 18, 2192–2196.
(65) Flory, P. J.; Fox, T. G. *J. Am. Chem. Soc.* 1951, 73, 1904.

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