Evolution of Composition, Molar Mass, and Conductivity during the Free Radical Copolymerization of Polyelectrolytes†

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Despite their importance in biological and technological contexts, copolymeric polyelectrolytes (or “copolyelectrolytes”) continue to present challenges to theorists and experimentalists. The first results of a unified approach to the kinetics and mechanisms of copolyelectrolyte synthesis and the physical characteristics of the resulting polymers are presented. The free radical copolymerization of 4-vinylbenzenesulfonic acid sodium salt and acrylamide was monitored using automatic continuous online monitoring of polymerization reactions (ACOMP), from which the average bivariate composition and mass distributions were determined. Composition drift was related to the evolution of conductivity. In some cases bimodal populations of copolyelectrolyte and homopolymeric poly(acrylamide) resulted, i.e., blends of copolyelectrolyte and neutral homopolymer. The end-product scattering behavior depended on whether the end-product was bimodal or not, as demonstrated using automatic continuous mixing (ACM) in conjunction with light scattering and viscosity. Negative light-scattering third virial coefficients were found for bimodal end-products. This combined approach may allow connecting the synthesis kinetics to the resulting “trivariate” distribution of composition, molar mass, and linear charge density, which in turn controls the properties of end-product solutions, such as chain conformations, interparticle interactions, viscosity, interactions with colloids and other polymers, phase separation, etc. Unified results may allow testing and improvement of existing polyelectrolyte theories, development of new quantitative physicochemical models, provide advanced characterization methods, set the stage for studying more complex copolyelectrolytes, such as hydrophobically modified ones, and provide tools for ultimately controlling and tailoring the synthesis and properties of copolyelectrolytes.

Introduction

In this work new analytical tools allow a unified approach to understanding copolyelectrolytes. Copolyelectrolytes combine the functional characteristics of copolymers with the unusual properties of polyelectrolytes. Copolyelectrolytes are copolymers in which at least one of the comonomers is electrically charged.

Post-polymerization analysis for determining the copolymer bivariate mass/composition distribution currently relies on complicated, tedious cross-fractionation and other coupled techniques. These include calorimetry and densimetry,¹ liquid chromatography,² temperature rising elution fractionation,³⁴ crystallization analysis fractionation,⁵ and techniques involving multidetector SEC alone,⁶ SEC/NMR,⁷ SEC/MALDI,⁸ and SEC/thin layer chromatography.⁹¹²¹³ Chromatographic techniques for composition analysis were recently reviewed.¹⁴

Long-range electrostatic forces are preeminent in polyelectrolytes. At very low ionic strength (IS), there are strong interparticle correlations that lead to angular scattering peaks of neutrons,¹⁵⁻¹⁷ X-rays,¹⁸ and light,¹⁹⁻²² including under shear.²³ The ability to screen these effects with ionic strength (IS) increases, electrostatic excluded volume (EEV) and

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TABLE 1: Combined ACOMP/ACM Results for VB/AaM Copolymers

<table>
<thead>
<tr>
<th>expt. #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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</thead>
<tbody>
<tr>
<td>VB% (M)</td>
<td>0</td>
<td>10</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>dn/dc (cm²/g)</td>
<td>0.163</td>
<td>0.148</td>
<td>0.157</td>
<td>0.173</td>
<td>0.172</td>
<td>0.171</td>
</tr>
<tr>
<td>( A_1 ) (cm² mol⁻¹ g⁻²)</td>
<td>0.0073</td>
<td>−0.0974</td>
<td>−0.2442</td>
<td>1.0455</td>
<td>1.1027</td>
<td>1.0853</td>
</tr>
<tr>
<td>( A_2 ) (cm² mol⁻¹ g⁻²)</td>
<td>4.69 × 10⁻⁴</td>
<td>1.90 × 10⁻⁴</td>
<td>4.89 × 10⁻⁴</td>
<td>5.78 × 10⁻⁴</td>
<td>3.23 × 10⁻⁴</td>
<td>2.71 × 10⁻⁴</td>
</tr>
<tr>
<td>([\eta]_w) ACOMP 0.100M NaCl</td>
<td>130</td>
<td>122</td>
<td>184</td>
<td>333</td>
<td>393</td>
<td>440</td>
</tr>
<tr>
<td>([\eta]_w) ACM 0.100M NaCl</td>
<td>128</td>
<td>70</td>
<td>60</td>
<td>95</td>
<td>127</td>
<td>140</td>
</tr>
<tr>
<td>( M_w) SEC</td>
<td>459 000</td>
<td>NA</td>
<td>179 000</td>
<td>309 000</td>
<td>425 000</td>
<td>702 000</td>
</tr>
</tbody>
</table>

* C_{reactor} = 0.3636 M, 0.100 M NaCl in reactor and ACOMP detectors. ACM experiments listed here were done in 0.010M NaCl solutions. SEC solvent: 0.100 M NH₄NO₃+0.2 g/L NaN₃.

It is interesting to compare ACOMP with in situ methods such as NIR and Raman. While ACOMP gives the comonomer conversions, which those techniques also do, ACOMP additionally monitors the evolution of weight average molar mass \( M_w \) and weight average intrinsic viscosity, \([\eta]_w\). An advantage of Raman and NIR compared to ACOMP is that probes for the former can often be put inside the reactor, avoiding ACOMP’s complex withdrawal, dilution, and conditioning steps. The in situ probes also eliminate the delay times inherent to ACOMP. On the other hand, whether a probe is inserted into a reactor or a tube for withdrawal is inserted for ACOMP, access into the reactor is required in either case, and hence all techniques are “invasive” to this degree. Furthermore, probes inside of reactors can easily foul and lead to erroneous data. Working at high concentrations in the reactor normally requires that empirical models and calibrations be used to interpret in situ data. In fact, calibration difficulties with Raman are well-known, and whole articles are devoted to them. It is interesting to compare ACOMP with in situ methods such as NIR and Raman. While ACOMP gives the comonomer conversions, which those techniques also do, ACOMP additionally monitors the evolution of weight average molar mass \( M_w \) and weight average intrinsic viscosity, \([\eta]_w\). An advantage of Raman and NIR compared to ACOMP is that probes for the former can often be put inside the reactor, avoiding ACOMP’s complex withdrawal, dilution, and conditioning steps. The in situ probes also eliminate the delay times inherent to ACOMP. On the other hand, whether a probe is inserted into a reactor or a tube for withdrawal is inserted for ACOMP, access into the reactor is required in either case, and hence all techniques are “invasive” to this degree. Furthermore, probes inside of reactors can easily foul and lead to erroneous data. Working at high concentrations in the reactor normally requires that empirical models and calibrations be used to interpret in situ data. In fact, calibration difficulties with Raman are well-known, and whole articles are devoted to them.

The current work characterizes the origins of some copolyelectrolyte properties, by combining recent advances in ACOMP with polyelectrolyte equilibrium characterization using automatic continuous mixing (ACM). The main thrust is to follow the effects of the kinetics of synthesis on the characteristic distributions and the effects of these distributions on the solution properties of the final copolyelectrolyte end-product. While the experimental trail is set out in this work connecting synthesis with some end-product solution behavior, a full theoretical unification will require considerable work.

**Experimental Methods**

Acrylamide (Aam) and 4-vinylbenzenesulfonic acid sodium salt (VB) were obtained from Fluka. Copolymerizations were initiated in aqueous solution at 60 °C, with 2,2'-Azobis(2-amidinopropane)dihydrochloride (V50). Different values of IS in the reactor were used for different reactions, although the majority of results presented here were carried out in 0.100M NaCl in the reactor. A total monomeric concentration, the sum of VB and Aam, of 0.364M was used in all experiments.

The ACOMP procedure involved continuous withdrawal of a small stream of reactor solution (0.1 mL/min), with a 2% dilution in the first dilution stage in a low-pressure mixing chamber, followed by different ratios of dilution in the second stage, in a high pressure mixing chamber, to produce a total solution concentration of ~0.4 mg/mL in the detector train. Each dilution stage was made with in 0.100 M NaCl aqueous solvent. The detector train included a dual wavelength UV spectrophotometer (a Shimadzu AV-10vp operating at 206 and 260 nm), custom-built capillary viscometer, Waters 410 refractive index detector (RI), and a custom built multi-angle light scattering unit. A conductivity probe (YSI 32, Yellow Springs Instruments Co., Inc.) was inserted in the reactor, and its signals captured with those from the other instruments via an Analog Digital converter.

The polyelectrolyte properties of the evolving copolymer could be enhanced by using a lower IS in the ACOMP diluent, i.e., using lower IS leads to more pronounced changes in light scattering and viscosity due to less suppression of electrostatic effects. This is not pursued here. It is emphasized, however, that all experiments in ACM and ACOMP use high enough IS for detection that polyelectrolyte effects commonly observed at very low IS are not manifest, i.e., the electroviscous effect and angular scattering maxima, which in dilute solutions normally are observed below IS of 0.001 M.

**Results and Discussion**

Figure 1 shows raw data for a 10/90 (%) ([VB]/[Aam]) copolymerization reaction in aqueous 0.0002 M NaCl and 0.364 M total comonomer. After solvent baseline stabilization, Aam was added, and the UV206 nm signal increased. With subsequent addition of VB, both UV signals and conductivity \( \sigma \) increased. The UV extinction coefficients for Aam and VB were determined from the UV detector response to their stepwise additions, and used subsequently to compute the concentration of each comonomer during the reaction by solving the two simultaneous...
respectively. Signals serve as visual guides to Aam and VB conversion, and PAM homopolymer was produced.

206 nm signal. Hence, inadvertently, a blend of copolyelectrolyte and PAM homopolymer was produced.

First-order fashion during the first phase of the reaction, seen by the 260 nm signal. After VB was exhausted, the remaining Aam homopolymerized rapidly; both phases can be seen in the 206 nm signal. Hence, in Figure 3 the latter condition occurs up to \( f_{\text{VB}} = 0.45 \), which is near the \( f_{\text{VB}} \) value where CC occurs, however, \( \sigma \) decreases more per charged monomer linked into copolymer chains.

The figure also shows the cumulative weight averaged mass, \( M_w, \) and \( M_{w,\text{inst}} \), respectively, for experiment #2 (not Figure 1 data).

When the reactor temperature reached 60 °C, initiator was added (15 000 s). VB was copolymerized faster than Aam in first-order fashion during the first phase of the reaction, seen by the 260 nm signal. After VB was exhausted, the remaining Aam homopolymerized rapidly; both phases can be seen in the 206 nm signal. Hence, inadvertently, a blend of copolyelectrolyte and PAM homopolymer was produced. \( \sigma \) decreased as VB was incorporated into copolyelectrolyte in the first phase, and remained constant in the second phase of Aam homopolymerization.

Figure 2 shows the fractional conversion of each comonomer, \( f_{\text{VB}} \) and \( f_{\text{Aam}} \), respectively, for the same reaction in 0.100 M NaCl, obtained from the dual wavelength UV data. The two-phase behavior of \( f_{\text{Aam}} \) is striking. Its polymerization rate increases when the VB is exhausted.

The high initial slope of \( \sigma \) versus \( f_{\text{VB}} \) in Figure 3 suggests significant CC early in the reaction. The average spacing between VB monomers on the chain is \( \xi \approx \frac{d}{Z_{\text{inst,VB}}} \), where \( d \) is the monomer contour length, \( \approx 0.26 \text{ nm} \). A dimensionless length scale \( \xi/Z \) gives the average number of \( \xi \) between VB monomers. For \( \xi/Z < 1 \), when CC is expected, \( Z_{\text{inst,VB}} > 0.36 \). Hence, in Figure 3 the latter condition occurs up to \( f_{\text{VB}} = 0.45 \), which is near the \( f_{\text{VB}} \) value where \( \sigma \) decreases more per charged monomer linked into copolymer chains.

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Not all starting ratios of \([\text{VB}] / [\text{Aam}] \) led to blends of copolyelectrolyte and neutral homopolymer, polyacrylamide (PAM). Figure 4 contrasts the cases of 10/90, 25/75, 50/50, and 75/25 (%). For the first case, already seen above, and the second, the two phase conversion of Aam results, whereas in the latter two cases, there is only a single phase of conversion for both Aam. The inset shows that VB has a single phase of conversion in each experiment, but in the latter cases it is not exhausted, and continues to co-convert with Aam throughout the reaction; i.e. no blend is produced. The two-phase acrylamide conversion
It is emphasized that all the data presented here are model-independent, including the striking two-phase copolymerization kinetics. Traditionally, different models for reactivity ratios (RR) have been used to interpret kinetics and composition distributions. In fact, an extended numerical error in variable method was developed to obtain RR from ACOMP and applied to methyl methacrylate/styrene copolymerization. The authors are separately analyzing the current data, with tentative values of $r_{Aam} \approx 0.18$, $r_{NaSS} \approx 2.0$ in 0.100M NaCl. There is also strong evidence of implicit penultimate effects including for terpolymerization reactions.

**End-Product Characterization by ACM. Light Scattering.**

The trivariate distribution produced during copolyelectrolyte synthesis should control end-product solution behavior. Light scattering at low to moderate IS can be dominated by second and third virial coefficients $A_2$ and $A_3$, respectively. Extensive theories for $A_1$ have been developed for monodisperse chain polymers. A theoretical quantity of interest is

$$g = \frac{A_3}{MA_2^2} \quad (3)$$

For hard spheres $g = 5/8$, whereas for coil polymers, measured values typically range from 0.15 to 0.56. This range of values has typically been found in low to moderate polydispersity polymers. Monte Carlo simulations yielded a “universal” asymptotic value at large M of 0.30. Nearly constant values of $g$ for linear sodium hyaluronate was found over a wide range of IS. Stockmayer and Casassa pointed out early on that in polydisperse (including bimodal) solutions the values of $A_2$ and $A_3$ measured by light scattering are not the same as those found in the usual expansion for osmotic pressure, so that caution must be used when comparing these quantities.

For the bimodal end-products the ACM results lead quickly to the frontier of both experimental and theoretical knowledge. Experiments show that definitive theories for cross-species interactions are quite incomplete, even for simple mixtures of two monodisperse, neutral polymers of the same species but different mass (e.g., polystyrene in toluene).

Multicomponent scattering formalisms can be invoked for the case of multiple interacting polymer species. One approach for a system of two distinct polymers a and b gives

$$I_{\text{total}} = S_{ab}(q)P_a(q)K_{ab}M_a + 2S_{ab}(q)P_a(q)K_{ab}M_aP_b(q)K_{bc}M_b + S_{ab}(q)P_b(q)K_{bc}M_b$$

for which there are theories to model intraparticle form factor $P(q)$, and interparticle structure factors $S_{gab}(q)$. In this case is the excess Rayleigh scattering ratio (cm$^{-1}$), and $K$ for each species is the usual optical constant, which for vertically polarized incident light is $K = 4\pi^2n^2(dn/dc)^2/N_{\lambda}$.4

Figure 6 shows $Kc/H(q = 0)$ versus polymer concentration at different IS, from ACM for the copolyelectrolyte/neutral polymer blend produced at 0.100M NaCl. I is the Rayleigh scattering ratio (in cm$^{-1}$). At $q = 0$, $P(q) = 1$ for each...
potential at high IS. It is noted that just because progressively screened with salt, leaving only the steric repulsion cross-terms between the copolyelectrolytes and the neutral PAM components; e.g., one may surmise a polyion interaction with regions of potential. The negative $A_3$ may reflect attractive interactions between polymers have little effect on how they hydrodynamically perturb the fluid velocity flow field around each other, and hence do not create large interparticle effects at the low concentrations used here. Light scattering is much more sensitive to “soft” interpolymer interactions, such as the electrostatic interaction, since the virial coefficients integrate whatever interparticle potentials exist over all spatial separations experiments it was found that sodium hyaluronate mixed with PAM gives the same $A_2$ and $A_3$ trend as the VB/Aam case. It is beyond the scope of this work to find a theoretical resolution of the observed behavior of equivalent $A_3$ for mixtures of polyelectrolytes and neutral polymers. The combined ACOMP and ACM methods, however, provide an experimental means for exploring this complex issue.

Reduced Viscosity. In contrast to the light scattering data, the reduced viscosity, $\eta_\text{r}$, data present no unusual behavior. Figure 8 shows $\eta_\text{r}$ versus $c$ at IS = 0.010 M for the end-products from the Table 1 reactions. These all yield the usual linear behavior, with very small slopes over the range of measurement. The slope measures the intermolecular hydrodynamic interactions and there are no qualitative changes between bimodal and unimodal end-products. The variations in the $c = 0$ intercept, which equals $[\eta]_\text{w}$, are due both to the molar mass differences of the samples, and their $\xi$ distributions.

This behavior is rationalized as follows: Intramolecular electrostatic interactions can strongly affect the dimensions of polyelectrolytes, and hence their $[\eta]_\text{w}$, but purely electrostatic interactions between polymers have little effect on how they hydrodynamically perturb the fluid velocity flow field around each other, and hence do not create large interparticle effects at the low concentrations used here. Light scattering is much more sensitive to “soft” interpolymer interactions, such as the electrostatic interaction, since the virial coefficients integrate whatever interparticle potentials exist over all spatial separations.
Figure 9. $\eta_v$ vs $c$ at IS = 0.010 M for different end-products. Top frame shows the exponent $b$, in the pseudoscaling log($\eta_v$) vs log(IS).

between pairs of particles. Hence, the changes in light scattering behavior due to interactions is much more striking than those for viscosity.

$[\eta]_w$ has interesting behavior versus IS. For each end-product $[\eta]_w$ was determined at IS = 0.010, 0.100, and 0.300 M. While no simple power law is expected to relate $[\eta]_w$ versus IS, using these three points and fitting a pseudo-power law of the form $[\eta]_w \approx aIS^b$ yields the exponents for $b$ as a rough and ready indicator of how the end-product $[\eta]_w$ reacts to IS. The values of $b$ are shown in the Figure 8 inset. For PAM $b$ is close to zero, as expected, and $b$ levels out at 0.35 for VB% $\geq 50$%: i.e., this is consistent with the notion that for a high % of VB in the chains, CC will limit $\xi$ to $\approx 1$, so that there will be no difference in the $\xi$ distribution above this threshold. This theoretical conclusion is supported by the Figure 8 inset. If the higher percentage VB end-products had higher $\xi$, then $b$ would continue to decrease with $\xi$, instead of leveling off.

Summary

It has been demonstrated that ACOMP can be used to follow the evolution of the average bivariate composition/molar mass distribution during synthesis of copolyelectrolytes, and that under relatively low starting percentages of VB bimodal end-products are produced, which are blends of copolyelectrolyte and neutral homopolymer (PAM). The conductivity monitoring shows a strong correlation between its decrease and incorporation of VB, and it ceases to change once VB is fully consumed in the bimodal reactions. The relationship between conductivity changes with conversion and the evolution of the $\xi$ distribution are complex, involve many factors, and are beyond the scope of this initial study.

The end-product characterization using ACM shows dramatically different behavior between those end-products that are bimodal and those that are not. In the former case $A_2$ is actually negative at low IS, whereas $A_2$ is always positive for all end-products at all IS. The negative $A_2$ is surmised to be related to an attractive ion-dipole interaction between the neutral polymer and the copolyelectrolyte in the bimodal populations. This interaction is screened away at high IS leaving $A_3$ positive. Experimental proof that this behavior is due to interactions between the bimodal populations is yielded by using deliberate blends of neutral polymer and copolyelectrolyte, where it was possible to again obtain negative $A_3$ at low IS. The reduced viscosity behavior is entirely insensitive to these soft interchain interactions, and no striking differences are found between unimodal and bimodal end-products. On the other hand, the relationship between $[\eta]_w$ and IS for the different end-products supports the notion that counterion condensation limits the linear charge density for copolyelectrolytes with high levels of VB.

It is hoped that this approach will lead to better theoretical understanding of the kinetics of copolyelectrolyte synthesis, polyelectrolyte properties, especially scattering behavior, and provide a practical means of controlling the distributions to produce polyelectrolytes of desired properties.

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References and Notes

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