Cationic Copolyelectrolytes: Online Monitoring of the Synthesis and Subsequent Copolymer Characterization

Zheng Li, Alina M. Alb*

Kinetics of copolymerization reactions of diallyldimethylammonium chloride (DADMAC) and dimethyl acrylamide (DMA) in aqueous solvent is studied, with highlights on features that control many aspects of the polymeric materials behavior throughout and post-synthesis. The aim of this study is twofold; first, to offer a method to study the impact of the incorporation of the cationic DADMAC on the composition drift, molecular mass of the copolyelectrolyte, and on the polyelectrolyte behavior by monitoring in real time the copolymerization reactions with a neutral monomer under different conditions. Additionally, it is meant to make the transition toward the next step, controlling the reaction kinetics during designed semi-batch experiments designed to achieve the average mass and composition distributions desired.

1. Introduction

Water-soluble synthetic polyelectrolytes are of interest due to their multiple applications in fields such as water purification, paper production, optoelectronics, and biotechnology. Their applicability is enhanced by the ability to control composition distribution, charge density, and molecular weight, which offers options in designing copolymeric polyelectrolytes (or “copolyelectrolytes”) with a wide variety of functions.

It is known that the polymerization of ionic monomers in aqueous solution is strongly affected by electrostatic interactions. [1–4] Besides contributing to the electrostatic driving force, the polyelectrolyte charge density also introduces electrostatic repulsions between charges along the polyelectrolyte backbone that act to expand or stiffen the molecular conformation of the chain in solution. [5]

The ability to screen these effects with ionic strength leads to dramatic changes in polyelectrolyte properties. [6, 7]

Several theories have been successful in unifying these phenomena. [8–10]

With the availability of novel charged monomers, copolyelectrolyte synthesis and characterization attracted more interest, despite challenges encountered. [11–16]

Studies on the effects of ionic strength and initial monomer composition on reaction kinetics have been reported for diallyldimethylammonium chloride (DADMAC) and other charged monomers. [17–24]

Experimental approaches to determine important copolymer features controlling many aspects of the polymeric materials behavior, such as the bivariate composition and mass distribution involve usually complementary techniques. [25–28]

Kinetics of copolymerization reactions of two comonomers with widely different reactivity ratios, DADMAC and dimethyl acrylamide (DMA) in aqueous solvent were studied in this work by following online polymerization reactions. The goals of this study are to assess the impact of the incorporation of the cationic DADMAC on the
composition drift, molecular mass of the copolyelectrolyte, and on the polyelectrolyte behavior and thus to make the transition toward the next step, controlling the reaction kinetics and copolymer composition during designed semi-batch experiments.

Given the reported facts that the allyl group in DADMAC leads to rather low co-monomer conversion compared with other cationic monomers,[7] it is hoped that the knowledge and possibility of controlling the relationship between composition and polymer properties will allow maximizing the efficiency of the cationic monomer in the copolymer. In the same time, the choice of DADMAC allows comparison with previous studies.

Additionally, it is intended, by combining online and post-polymerization techniques, to offer a complete characterization of the synthesized copolymers, illustrated in the evolution of virial coefficients and intrinsic viscosity, and rationalized through electrostatic persistence length and electrostatic excluded volume effects.

2. Experimental Section

2.1. Materials

The monomers, DADMAC (65 wt% in water) and DMA (99%), and the initiator, 2,2’-azobis(2-methylpropionamidine)dihydrochloride (V50) were used as received from Aldrich.

2.2. Synthesis

All the reactions were carried out at 60 °C in a 250 mL three-neck round bottom flask reactor equipped with a condenser, under nitrogen flow, with a total of ≈5.5% monomer by mass, in water.

2.3. Measurements

The copolymerization reactions were followed in real time using automatic continuous monitoring of polymerization reactions (ACOMP),[29,30] a non-chromatographic method that relies on continuous extraction and dilution of a small stream of reactor contents on which measurements are made, as the reaction proceeds. Detector train contained a single capillary viscometer, a multi-angle light scattering detector (Brookhaven, BI-Mwa), a refractive index detector, and a UV–Vis spectrophotometer (Shimadzu). Data were collected every 2 s, with a 20 min delay time between reactor extraction and detector measurements. While the synthesis was made in water, dilution throughout online monitoring of the reactions was made with 0.1 M NaCl, chosen to largely suppress the polyelectrolyte properties of the copolymers.

Endproduct polymer characterization was made by automatic continuous mixing (ACM) means.[31] The technique used a Shimadzu HPLC pump, connected to a mixing unit, and same detectors as in ACOMP.

Multidetector size-exclusion chromatography (SEC) was carried out offline in aqueous solvents at different ionic strengths using same detectors as in ACOMP. Shodex SB-804 HQ with 0.1 M NaCl as eluent was used to follow monomer conversion, whereas SB-804 HQ and SB-806 HQ in series were used to determine copolymer MWD and molar-mass dispersity, D_m, with 1 M NaNO_3 as eluent.[32]

Additionally, 1H NMR and thermogravimetric analysis (TGA) experiments were made. 1H NMR were conducted on a Bruker Avance 300 NMR Spectrometer with the frequency of 75 MHz. TGA experiments were made on a TGA 2850 from TA instrument. The degradation profiles were recorded from 25 to 600 °C at a heating rate of 5 °C min⁻¹.

3. Results and Discussion

3.1. Reaction Kinetics and Polymer Characterization During Online Monitoring of the Synthesis

In agreement with previously reported data on reactivity ratios of DADMAC and DMA,[33–35] it was found that DMA was incorporated in the copolymer chains at a much faster rate than DADMAC. After DMA was exhausted, the remaining DADMAC continued to polymerize, leading to a blend of DMA–DADMAC copolyelectrolyte (rich in DMA) and DADMAC homopolymer to be produced.

Table 1 offers a summary of the copolymerization reactions, along with experimentally determined characteristics during the synthesis. In this work, all concentrations involving composition and sequence length distributions are in molar concentration (mol L⁻¹); for example, [DMA], whereas in dealing with light scattering and viscosity, mass concentration are used (g cm⁻³); for example, c_{DMA}. Similarly, in the case of comonomer conversion, f is used for fractional molar monomer conversion and p for conversion by mass.

3.1.1. Online Data

Continuous data gathered by the online monitoring detection platform allowed model-free physical quantities such as comonomer conversion, composition drift, copolymer mass, and reduced viscosity to be determined as the polymerization occurs and thus, offered the means for polymer characterization during the synthesis. An example is given in Figure 1, which shows raw data collected by ACOMP for reaction C, Table 1. Light scattering (shown at 90°, LS90°), UV absorbance at 260 nm (UV@260nm), refractive index (RI), viscosity, and temperature signals are shown. First, 0.1 M NaCl was pumped through the detectors. The two
monomers were then added sequentially and the RI and UV response to their addition allowed refractive index increments (\(dn/dc\)) and extinction coefficients to be computed. As soon as the temperature reached the preset value (60 °C), V50 was added and the reaction has started. As shown by the increase in the temperature at the onset of the reaction, due the higher amount of DMA in the initial composition, the copolymer chains richer in DMA produced lead to a slight Tromsdorff effect.[36] This effect is less significant for reactions with a smaller DMA amount in the starting composition. The decrease in the UV signal at 260 nm followed DMA consumption whereas the steady increase in RI, viscosity and light scattering data throughout the reaction indicated the copolymer production. Samples from the waste line were taken periodically and injected into SEC unit in order to follow DADMAC conversion and confirm online results.

3.1.2. Comonomer Concentration and Conversion

Continuous UV data collected during online monitoring of the polymerization reactions were used together with UV&RI discrete data from SEC to calculate DMA and DADMAC concentrations, respectively. Additionally, \(^1\)H NMR measurements were made on samples withdrawn during reactions, as an independent cross-check method to determine comonomer concentrations, found in excellent agreement with those provided by ACOMP and SEC.

As mentioned above, an interesting feature was observed in the evolution of the DADMAC–DMA monomer pair, as soon as DMA was finished, DADMAC continued to polymerize with a different rate, leading to a blend of DMA–DADMAC copolymer chains and chains containing mostly DADMAC homopolymer. This gives an opportunity to control the incorporation of the comonomers and maximize their efficiency in future work, according to the polymer applications.

The two-stage trend in the monomer evolution, result of the differences in the monomer propagation rate coefficients as the monomer composition changes throughout the reaction, is illustrated in Figure 2, where comonomer conversions, \(f_{\text{DADMAC}}\) and \(f_{\text{DMA}}\), and total fractional molar conversion, \(f\), are shown as functions of time for several copolymerization reactions, shown in Table 1. A general trend, expected considering the low reactivity of DADMAC, is that higher DADMAC percentage in the initial composition leads to a decrease in the reaction rate. The common feature of the conversion data, the bimodal behavior, becomes less apparent for reactions with lower DMA content in the starting composition, due to the higher DADMAC incorporation in the copolymer chains. This also leads to a longer copolymerization regime, until
DMA gets entirely consumed. Both continuous ACOMP and discrete SEC data shown in the figure are in good agreement.

### 3.1.3. Composition Drift and Sequence Length Distribution

The effect of the initial composition on comonomer incorporation in the copolymer chain. The very different incorporation of the two comonomers in the copolymer chains was quantified and expressed in a more illustrative way by following the copolymer composition drift during synthesis, $F_{\text{inst}}$. It is important to mention that the knowledge of the composition at any time during the reaction eliminates the need to compute the model dependent reactivity ratios. Both continuous and discrete measurements on comonomer concentrations were used to compute the average instantaneous molar fraction of DADMAC in the copolymer chain formed at any given moment based on Equation (1):

$$F_{\text{inst,DADMAC}} = \frac{d[D\text{ADMAC}]/dt}{d[D\text{ADMAC}]/dt + d[D\text{MA}]/dt} \quad (1)$$

Figure 3 shows the instantaneous DADMAC composition drift, $F_{\text{inst,DADMAC}}$ versus total fractional molar conversion $f$ for a series of copolymerization reactions with different initial composition, reactions C-F, Table 1. Continuous data points were computed from online concentration data, while the discrete points were from SEC measurements. In all the reactions, DMA polymerizes at much faster rate, leading to copolymer chains with low DADMAC content. Thus, $F_{\text{inst,DADMAC}}$ shows a slow increase with conversion during this regime but changes dramatically as DMA becomes less available and more DADMAC is incorporated in the copolymer chains, which become progressively richer in DADMAC or containing only DADMAC toward the end of the reaction.

While the knowledge of the composition drift provides important information on the copolymers compositional heterogeneity, it reveals nothing about their sequence distribution, important in determining different aspects of the copolymer behavior.

The instantaneous sequence length distribution, defined as the probability of having a sequence of $k$ monomers in a row of type A, followed by a monomer B can be determined from ACOMP measurements at each point $f$.\(^{[37,38]}\) The instantaneous number-average sequence length of DMA and DADMAC, respectively, was computed on the basis of Equation 2 and 3, with $r_{\text{DMA}} = 6.3$ and $r_{\text{DADMAC}} = 0.3$ used for the comonomer reactivity ratios.\(^{[19]}\)

### Table 1. List of polymerization reactions, together with reaction rate constant, $\kappa$, comonomer conversions by mass, $p_{\text{DADMAC}}, p_{\text{DMA}}$, total conversion by mass, $p_t$, and weight average-molecular weight, $M_w$ (at the end of reaction). For all reactions, total monomer molar concentration, $[M] = 0.5$ \text{M} and initiator concentration, $[I] = 0.005$ \text{M} were used.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>DADMAC/DMA [M/M]</th>
<th>$\kappa^{a)}$ [10$^{-4}$ s$^{-1}$]</th>
<th>$p_{\text{DADMAC}}$</th>
<th>$p_{\text{DMA}}$</th>
<th>$p_t$ [10$^5$ g mole$^{-1}$]</th>
<th>$M_w$ [10$^5$ g mole$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0/100</td>
<td>NA</td>
<td>NA</td>
<td>1</td>
<td>1</td>
<td>11.0</td>
</tr>
<tr>
<td>B</td>
<td>10/90</td>
<td>9.08</td>
<td>53</td>
<td>1</td>
<td>0.93</td>
<td>5.5</td>
</tr>
<tr>
<td>C</td>
<td>20/80</td>
<td>7.10</td>
<td>40</td>
<td>1</td>
<td>0.83</td>
<td>4.3</td>
</tr>
<tr>
<td>C$^{b)}$</td>
<td>20/80</td>
<td>7.09</td>
<td>40</td>
<td>1</td>
<td>0.82</td>
<td>4.8</td>
</tr>
<tr>
<td>D</td>
<td>30/70</td>
<td>6.21</td>
<td>37</td>
<td>1</td>
<td>0.71</td>
<td>3.5</td>
</tr>
<tr>
<td>E</td>
<td>40/60</td>
<td>4.21</td>
<td>40</td>
<td>1</td>
<td>0.68</td>
<td>2.2</td>
</tr>
<tr>
<td>F</td>
<td>50/50</td>
<td>3.49</td>
<td>31</td>
<td>1</td>
<td>0.56</td>
<td>2.0</td>
</tr>
<tr>
<td>G</td>
<td>100/0</td>
<td>NA</td>
<td>26</td>
<td>NA</td>
<td>0.26</td>
<td>NA</td>
</tr>
</tbody>
</table>

$^{a)}$from first-order function fits to total mass conversion; $^{b)}$reaction made in 0.1 \text{M} NaCl.

![Figure 3](https://www.MaterialsViews.com)  
Figure 3. $F_{\text{inst,DADMAC}}$ versus total fractional molar conversion, $f$ for copolymerization reactions C-F, Table 1.
\[ N_{A/n}(f) = \frac{1}{1 - W_{AA}(f)} \]  

(2)

where \( W_{AA} \) is the probability that the propagating radical of monomer A, adds to A

\[ W_{AA}(f) = \frac{r_A y_A(f)}{y_A(f)(y_A - 1) + 1} \]  

(3)

\( r_A \) is the reactivity ratio of monomer A, and \( y_A \) is the mole fraction of monomer A, at any instant.

Shown in Figure 4 are computed number-average sequence length of the comonomers, \(<N_{DMA}>_n\) and \(<N_{DADMAC}>_n\), for several copolymerization reactions with different initial compositions (B-F, Table 1). The addition of DADMAC monomer units into the copolymer chains is dictated by both reactivity ratio difference and initial comonomer composition. Thus, the evolution of \(<N_{DMA}>_n\) with conversion — shown in the left side of the figure — shows that the more DMA available, the longer sequences of DMA units are contained in the copolymer chains. The decrease with conversion corresponds to the depletion of DMA and the progressive addition of DADMAC. In the case of the reactions with less DMA in the starting composition, the addition of DADMAC is more favored at earlier conversion. The computed sequence length for DADMAC is shown in the right side of the figure. For each reaction, similar trends in the \(<N_{DADMAC}>_n\) evolution are observed: a slow increase throughout the copolymerization with DMA, followed by a significant jump, due to the DMA depletion. In these conditions, chains containing mostly or only DADMAC were obtained.

Despite the fact that DMA is favored to be incorporated in the copolymer chains, it is shown in the next sections that even in the case of the reaction with the least amount of DADMAC in the starting composition (10%), there are enough charged monomer units in the copolymer chains to confer the copolymer polyelectrolyte properties.

3.1.4. Molecular Weight and Reduced Viscosity

For homopolymers, the Zimm\(^{40}\) single contact approximation is generally used to determine \( M_w \). In this work, the computed mass comonomer concentrations are used together with data from light scattering measurements in the determination of \( M_w \) based on authors previous reported studies.\(^{41}\)

The effect of initial comonomer composition on the copolymer molecular weight is illustrated in Figure 5 for several copolymerization reactions with different initial composition. Thus, the higher amount of DMA in the initial composition led to bigger polymer molecular weight, reached at faster reaction rate. Typical trends for free radical polymerization reaction in the quasi-steady state approximation are also observed: longer chains at the beginning, followed by short chains as the monomer gets consumed.

Similar trends and dependence on both initial composition and comonomer incorporation, observed in the evolution of \( M_w \), were seen in the reduced viscosity, \( \eta_r \) behavior, shown in the figure for reactions B and F, Table 1. Reduced viscosity was computed at each moment \( t \), from the viscosity signals and concentration data based on the Equation 4:
in the copolymer chains and leads to more homogenous population, with a narrower mass distribution, as seen in the case of reactions E and F. The increase in $M_w / M_n$ with decreasing DADMAC fraction of copolymer is also shown in the figure.

The effect of the preferential comonomer incorporation in the copolymer chains on the evolution of MWD as the reaction occurred was also studied. Selected MWD data during copolymerization reactions with different initial composition are shown in Figure 8. For each reaction,
MWD corresponding to the time DMA was consumed and at the end of the polymerization reaction are shown. As seen in the case of the reactions B, C, and E and explained above, higher DMA amount available leads to bimodal and rather broad mass distributions. In the case of reaction F, the higher DADMAC percentage and no exothermic effects brought by DMA rapid polymerization, when present in high amount leads to a more homogeneous mass distribution, with a narrower breadth.

The bimodal behavior observed in the composition drift, which leads to a formation of a blend of copolymer and polyDADMAC was observed in TGA data, similar finding being reported by others.\textsuperscript{42–44} Figure 9 shows TGA curves for the endproducts of reactions B, C, E, and F in Table 1. The initial step of weight loss below 150 °C is due to the loss of water. Next stage, for temperatures between 175 and 280 °C, is the decomposition of unreacted DADMAC.\textsuperscript{45} The final stage, between 350 °C and 520 °C is due to the polymer decomposition. The percentage of weight loss from monomer increased from reaction B to F due to the higher amount of DADMAC in the initial composition and lower DADMAC conversion; the weight loss from polymer follows the same trend. The inset to the figure illustrates the evolution with \( T \) of \( \text{dw/dT} \), for temperatures corresponding to polymer decomposition. Broader temperature range of decomposition and a transition to bimodal are seen in the data from reactions B to E, as a shoulder builds at around 400–450 °C. This indicates the increase in the polyDADMAC chains after DMA was consumed, as DADMAC becomes richer in composition.

3.1.5. Effect of the Ionic Strength in Reactor on DADMAC Incorporation

Reported studies found that the addition of neutral low molecular salts led to an increase in polymerization rate.\textsuperscript{14,46–48} In this work, no significant effects on reaction kinetics were found, within the conditions studied.

3.2. Post-Reaction Polymer Characterization

Additional information on copolymers properties and the way they are influenced by ionic strength, depending on the initial composition and composition drift was obtained from ACM, which allowed physical quantities such as molecular weight, \( M_w \), second virial coefficient, \( A_2 \), radius of gyration, \( R_g \), and intrinsic viscosity, \( [\eta] \) to be determined.

A summary of ACM results from experiments for copolymer endproduct solutions in 0.1 M NaCl is given in Table 2. All data show the effect of the starting compositions on the copolymer characteristics: an increase in DADMAC percentage leads to higher \( A_2 \) and \( \kappa_H \) and lower \( M_w \) and \( MWD \) corresponding to the time DMA was consumed and at the end of the polymerization reaction are shown. As seen in the case of the reactions B, C, and E and explained above, higher DMA amount available leads to bimodal and rather broad mass distributions. In the case of reaction F, the higher DADMAC percentage and no exothermic effects brought by DMA rapid polymerization, when present in high amount leads to a more homogeneous mass distribution, with a narrower breadth.

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The behavior of $A_2$ is due to two effects: dependence on the mass and on the charge density. The high $A_2$ values for the endproducts of the reaction $F$ (50/50) and $G$ (0/100) suggest that the moderate ionic strength used (0.1 M NaCl) was not enough for a complete neutralization of the copolymer.

Table 3: $A_2$, $R_g$, $R_{g, Flory}$, and [η] values for copolymer endproduct solutions in H$_2$O and in 0.1 M NaCl.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_2$ [10$^{-4}$ mole cm$^3$ g$^{-2}$]</th>
<th>$R_g$ [nm]</th>
<th>$R_{g, Flory}$ [nm]</th>
<th>[η] [cm$^3$ g$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>in H$_2$O</td>
<td>in 0.1 M NaCl</td>
<td>in H$_2$O</td>
<td>in 0.1 M NaCl</td>
<td>in H$_2$O</td>
</tr>
<tr>
<td>B</td>
<td>9.40</td>
<td>4.08</td>
<td>57.0</td>
<td>47.9</td>
</tr>
<tr>
<td>C</td>
<td>13.2</td>
<td>2.99</td>
<td>76.7</td>
<td>38.5</td>
</tr>
<tr>
<td>D</td>
<td>16.9</td>
<td>2.96</td>
<td>49.5</td>
<td>40.3</td>
</tr>
<tr>
<td>E</td>
<td>17.7</td>
<td>4.86</td>
<td>54.8</td>
<td>39.0</td>
</tr>
<tr>
<td>F</td>
<td>35.8</td>
<td>9.60</td>
<td>53.9</td>
<td>29.2</td>
</tr>
</tbody>
</table>

From hydrodynamic point of view, typical polyelectrolyte behavior, characteristic to non-free draining limit, was observed with the increase in ionic strength: the repulsion from the like charges on the chains is reduced, leading to a decrease in viscosity.

3.2.2. Effect of the DADMAC Incorporation on the Polyelectrolyte Properties and Polymer Conformation

This section summarizes previous discussion and brings additional results to conclude findings on DADMAC effects on the copolymer behavior, in terms of polyelectrolyte behavior and chain stiffness.
At low ionic strength, polyelectrolytes display an extended, rod-like conformation in aqueous solution due to electrostatic charge repulsion along the polymer backbone and rearrangement of counterions. Dynamical behavior of semiflexible long-chain molecules in solution was studied. A convenient means to assess the flexibility of the copolymer chains is given by the use of the apparent persistence length, $L_p$, composed of an intrinsic persistence length and an electrostatic persistence length, which combines electrostatic stiffening and excluded volume in a single parameter, allowing chains of different mass to be compared. Good agreement between theoretical considerations and experimental results was reported.

Here, “apparent” $L_p$ values were computed based on the worm-like chain expression for a polymer chain with no excluded volume. The impact that additional DADMAC incorporation makes on the polyelectrolyte behavior and on the copolymer conformation is illustrated in Figure 12, which shows the evolution of $A_2$ and $L_p$, respectively, with $n_{DADMAC}$, for ACM experiments in $H_2O$ and in 0.1 M NaCl made on samples withdrawn, at different stages in conversion, during polymerization reactions with different initial comonomer composition; $n_{DADMAC}$ is defined as

$$n_{DADMAC} = \frac{[DADMAC]_0 \times f_{DADMAC}(t)}{[DADMAC]_0 \times f_{DADMAC}(t) + [DMA]_0 \times f_{DMA}(t)}$$  \hspace{1cm} (6)$$

where $[DADMAC]_0$ and $[DMA]_0$ are the initial molar concentration of the monomers, $f_{DADMAC}(t)$ and $f_{DMA}(t)$ are conversions at the time $t$ at which the polymer sample on which the measurement are made has been withdrawn from reactor.

As seen in the figure, the addition of NaCl leads to the decrease of the persistence length of the copolymer, resulting in a more random coil-like conformation of the polymer chains, similar to neutral polymers. This is seen also in the evolution of $A_2$ with increase of ionic strength and is due to the shielding of electrostatic interactions as effect of the reduction in the Debye screening length. In these conditions (in 0.1 M NaCl), there is no significant difference among the computed $A_2$ and $L_p$ values for the polymer samples with different amount of DADMAC in the copolymer chains.

Another way to illustrate the increase in the chain stiffness with the addition of DAMAC in the copolymer chain is by the use of the SEC-derived Mark-Houwink-Sakurada scaling law. In this work, the Mark-Houwink coefficients from power law fits to $R_g$ data versus copolymer mass indicate the transition from coil to a more extended conformation.

4. Conclusion

The use of the online monitoring technique to follow DADMAC–DMA copolymerization allowed kinetics of copolymerization reactions of two comonomers with widely different reactivity ratios to be studied. The impact of the incorporation of the cationic DAMAC on the composition drift, molecular mass of the copolyelectrolyte, and on
the polyelectrolyte behavior was quantified. This gives an opportunity to control the copolymer composition during designed semi-batch experiments and hence the material properties, according to the desired applications.

A quantitative polymer characterization was made by the use of several techniques. The effects of ionic strength and of the composition on the copolymer stiffness and polyelectrolyte behavior were studied and illustrated in the evolution of in $A_2$ and $\eta_\text{s}$, and rationalized through electrostatic persistence length and electrostatic excluded volume effects.

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