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Extrapolation Formulas for Dimensions of Branched Polyelectrolytes

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ABSTRACT: We have derived simple extrapolation formulas for the mean-square radius of gyration and structure factor of any branched polyelectrolytes for arbitrary values of molecular weight and various parameters of the screened electrostatic and excluded-volume interactions. In general, the mean-square radius of gyration $\langle S^2\rangle_b$ is proportional to $\kappa^{-4/5}L^{6/5}$ and L^2 in the strong and weak Coulombic screening limits, respectively, where κ is the inverse Debye length, L is the total chain length, and the proportionality coefficients depend on the nature and details of the branching. For uniform stars with f ($\gg$1) branches, $\langle S^2\rangle_b$ is proportional to $f^{-4/5}$ and $f^{-2/3}$ in the strong and weak screening limits, respectively. For uniform normal combs with p ($\gg$1) branch points, $\langle S^2\rangle_b$ is independent of p. Although $\langle S^2\rangle_b$ depends on κ to different extents for different values of κ, the ratio of $\langle S^2\rangle_b$ to the mean-square radius of gyration of a linear polyelectrolyte with the same molecular weight is independent of κ. This ratio is found to be independent of the nature and strength of the binary intersegment potential interactions, and its dependence on the branching architecture is derived.

Introduction

The characterization of the nature of branching in branched polymer molecules is an ongoing effort. The pioneering work of Zimm and Stockmayer[1] followed by a large literature[2,3] derived the mean-square radius of gyration $\langle S^2\rangle_b$ of molecules with specific branching in the absence of any excluded-volume effects. In this limit, $\langle S^2\rangle_b$ is proportional to the mean-square radius of gyration $\langle S^2\rangle$ of a linear molecule with the same number of segments as the branched molecule,

$$\langle S^2\rangle_b = g\langle S^2\rangle \tag{1}$$

For example, the proportionality constant g for uniform stars is given by

$$g = \frac{3f-2}{f^2} \tag{2}$$

where f is the number of branches in the star.

During the last decade, theories[4-7] have appeared which are relevant to the good solvent conditions. The relative success of different methods such as scaling arguments, renormalization group calculations, molecular dynamics simulations,[8] exact enumeration, and Monte Carlo techniques[9-11] in reproducing careful experimental results has recently been reviewed.[3] The essential result of these calculations is that, for uniform stars,

$$g(f) \equiv \langle S^2\rangle_b/\langle S^2\rangle \sim f^{-4/5} \tag{3}$$

in the limit of an infinite molecular weight and large number of branches in a very good solvent.

Although branched polyelectrolytes have been extensively used in the colloid industry, they have recently attracted careful experimental investigation, particularly in the context of electrophoresis.[12] In view of this we present here a self-consistent-field description of dimensions of branched polyelectrolytes. The formulas are derived for uniform stars, uniform combs, and rings, valid for arbitrary charge density on the chain backbone and Debye length. The extrapolation formulas presented here are approximate, and these are at the level of the critical size exponent for a chain in a good solvent being $^3/_5$ instead of 0.589 and the electrostatic interactions are assumed to be Debye–Hückel type. Yet these formulas are desirable to have, in view of the fact that it is difficult to perform a proper renormalization group calculation or computer simulations for polymers with long-range interactions.

The key result of this paper is the set of eqs 14–17. These equations completely give the mean-square radius of gyration of any branched polymer for arbitrary values of the parameters of the screened electrostatic interaction, the excluded-volume interaction, and the polymer chain. The two important ingredients are g and K (defined below) which are specific to the particular branching architecture. Two examples of branching, viz., uniform star and uniform normal comb and ring architecture, are considered in applying the general formulas. One of the main conclusions is that the ratio of the mean-square radius of gyration to that of a linear polyelectrolyte with the same molecular weight is independent of the nature of the intersegment interaction and depends only on the branching architecture.

Uniform Stars

Model. First we consider a polyelectrolyte with a uniform star configuration in a salt solution. The partition sum for this molecule with total contour length L and f branches of equal length L/f is given by the Edwards path integral,

$$Z = \int \prod_\alpha \mathcal{D}[\mathbf{R}_\alpha(s)] \exp\left\{-\frac{3}{2l}\sum_{\alpha=1}^{f}\int_0^{L/f} ds \left(\frac{\partial \mathbf{R}_\alpha(s)}{\partial s}\right)^2\right\} \times \exp\left\{-\frac{1}{2}\sum_\alpha\sum_\beta \int_0^{L/f} ds \int_0^{L/f} ds'\, V[\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s')]\right\} \times \prod_{\alpha=1}^{f} \delta(\mathbf{R}_\alpha(0)) \tag{4}$$

$\mathbf{R}_\alpha(s)$ is the position vector of the arc length variable s of the αth branch. l is the Kuhn step length. The term $\Pi_\alpha\delta$ gives the constraint that all branches are jointed at the origin. The symbol $\int\mathcal{D}[\mathbf{R}(s)]$ denotes functional integration representing the sum over all possible chain configurations. The potential interaction $V(r)$ between any two segments separated by a distance $\mathbf{r}$ is taken to be

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$$V(\mathbf{r}) = w\delta(\mathbf{r}) + \frac{w_c}{r}\exp(-\kappa r) \tag{5}$$

where $r = |\mathbf{r}|$. The first term on the right-hand side is the familiar excluded-volume effect, with wl^2 being the pseudopotential for the binary cluster integral. The second term on the right-hand side of eq 5 represents the screened electrostatic interaction between the polymer segments. $w_c = q^2/\epsilon k_B T$ where q is the charge per repeating unit of the chain, ϵ is the dielectric constant of the polyelectrolyte solution, k_B is Boltzmann's constant, and T is the absolute temperature. κ^{-1} is the Debye screening length and depends on the ionic strength of the solution.

Perturbation Theory. It is now straightforward to perform the perturbation theory to the leading order in V for any desired configurational property of the polymer. Since the details of such first-order calculations are well documented in the literature,[2,13-15] we merely give the result here. From eqs 4 and 5, the mean-square radius of gyration to the first order in perturbation theory is given by

$$\langle S^2\rangle_b = \frac{Ll}{6}g[1 + K(z + z_c) + ...] \tag{6}$$

where z and z_c are the dimensionless variables for the excluded-volume and screened Coulomb interactions, respectively, and are given by

$$z = (3/2\pi)^{3/2}wL^{1/2}l^{-3/2} \tag{7}$$

and

$$z_c = \frac{1}{15}\left(\frac{6}{\pi}\right)^{1/2} w_c L^{3/2} l^{-1/2} \left\{\frac{15\pi^{1/2}e^a}{2a^{5/2}}(a^2 - 4a + 6) \times \operatorname{erfc}(a^{1/2}) - \frac{3\pi}{a^{5/2}} + \frac{\pi}{a^{3/2}} + \frac{6\pi^{1/2}}{a^2}\right\} \tag{8}$$

where $a \equiv \kappa^2 Ll/6$. The details of the derivation of eq 8 are given in ref 15. The coefficient K was first calculated by Kron and Ptitsyn[13] and by Berry and Orofino[14] to be

$$K = \frac{3}{f^{1/2}(3f - 2)}\left[\frac{67.2^{7/2}}{315}(f - 1) - \frac{134}{315}(f - 2) + \frac{4}{45}(101.2^{1/2} - 138)(f - 1)(f - 2)\right] \tag{9}$$

g in eq 6 is the Zimm–Stockmayer result of eq 2.

Self-Consistent-Field Theory. The knowledge of the coefficient of the first-order perturbation theory can lead to approximate crossover formulas for $\langle S^2\rangle_b$ and the scattering structure factors for intermediate values of z and z_c if we adopt the self-consistent procedure originally invented by Edwards.[16] The starting point is to rewrite Z of eq 4 in terms of collective coordinates $\mathbf{R}(q)$ of the chain where q is the Fourier variable conjugate to the arc length variable,

$$Z = \int \prod_\alpha \mathcal{D}[\mathbf{R}_\alpha(q)] \exp\left\{-\sum_{\alpha=1}^{f}\int_{-\infty}^{\infty}\frac{dq}{2\pi}\frac{\mathbf{R}_\alpha(q)^2}{g_0(q)} - \frac{1}{2}\sum_\alpha\sum_\beta\int_0^{L/f} ds \int_0^{L/f} ds' \int \frac{d^3k}{(2\pi)^3}V_k \times \exp\left[i\mathbf{k}\cdot\int_{-\infty}^{\infty}\frac{dq'}{2\pi}(\mathbf{R}_\alpha(q')e^{iq's} - \mathbf{R}_\beta(q')e^{iq's'})\right]\right\} \tag{10}$$

where $\mathbf{R}_\alpha(s=0)$ is taken to be at the origin of the coordinate system for each α and V_k and $g_0(q)$ are given by

$$V_k = \left(w + \frac{4\pi w_c}{k^2 + \kappa^2}\right) \tag{11}$$

and

$$g_0(q) = 2l/3q^2 \tag{12}$$

By defining $g(q) = 2l_1(q)/3q^2$ such that Z is given by effective Gaussian distribution functions

$$Z = \int \prod_\alpha \mathcal{D}[\mathbf{R}_\alpha(q)] \exp\left\{-\sum_{\alpha=1}^{f}\int_{-\infty}^{\infty}\frac{dq}{2\pi}\frac{\mathbf{R}_\alpha(q)^2}{g(q)}\right\} \tag{13}$$

and determining $g(q)$ by extremizing the entropy of the branched polymer, we get (see section III of ref 15 for details)

$$\langle S^2\rangle_b = gLl_1/6 \tag{14}$$

where l_1 is given by

$$\left(\frac{l_1}{l}\right)^{5/2} - \left(\frac{l_1}{l}\right)^{3/2} = K[z + z_{c1}] \tag{15}$$

with

$$z_{c1} = \frac{1}{15}\left(\frac{6}{\pi}\right)^{1/2} w_c L^{3/2} l_1 l^{-3/2} \left\{\frac{15\pi^{1/2}e^{a_1}}{2{a_1}^{5/2}}({a_1}^2 - 4a_1 + 6) \times \operatorname{erfc}({a_1}^{1/2}) - \frac{3\pi}{{a_1}^{5/2}} + \frac{\pi}{{a_1}^{3/2}} + \frac{6\pi^{1/2}}{{a_1}^2}\right\} \tag{16}$$

and

$$a_1 = \kappa^2 Ll_1/6 \tag{17}$$

In obtaining these results approximations are made by taking the limit of $q \rightarrow 0$. The same result can be obtained by following the Edwards–Singh recipe[17] from the first-order perturbation theory.

Results. The explicit dependencies of l_1 on w, w_c, f, L, and κ are calculated using eqs 15–17. The limiting behaviors of these dependencies can readily be established. When only the excluded-volume effect is present ($w_c = 0$), eqs 15 and 7 lead, for $L \rightarrow \infty$, to

$$l_1 = l(Kz)^{2/5}, \quad w_c = 0 \tag{18}$$

so that it follows from eq 14 that

$$\begin{aligned}\langle S^2\rangle_b &= (1/6)Llg(Kz)^{2/5} \\ &= (1/6)(3/2\pi)^{3/5}g(wlK)^{2/5}L^{6/5}\end{aligned} \tag{19}$$

This contains the full dependence of f. If we take the ratio of $\langle S^2\rangle_b$ to the mean-square radius of gyration of a linear polymer with the same L, we get

$$g(f) \equiv \lim_{L\rightarrow\infty}\frac{\langle S^2(f)\rangle_b}{\langle S^2(f{=}1)\rangle_b} = 0.907gK^{2/5} \tag{20}$$

and for $f \gg 1$

$$g(f) \sim 1.942f^{-4/5} \tag{21}$$

The results of eqs 20 and 21 given in Table I are in close agreement with the experimental values reviewed in ref 3 and Monte Carlo estimates of Whittington *et al.*[9] for various values of f.

When the electrostatic interactions between segments are present, eqs 15 and 16 lead to the following limits in the absence of the excluded-volume effect. For strong

Table I. Dependence of the Ratio $g(f)$ of Uniform Stars on f for Different Conditions

f	good solvent ($wL^{1/2} \rightarrow \infty$)	strong screening ($\kappa(Ll_1)^{1/2} \rightarrow \infty$)	weak screening ($\kappa \rightarrow 0$)
1,2	1	1	1
3	0.783	0.783	0.787
4	0.638	0.638	0.646
5	0.539	0.539	0.552
6	0.467	0.467	0.483
12	0.269	0.269	0.294
18	0.194	0.194	0.220
∞	$\sim 1.942f^{-4/5}$	$\sim 1.942f^{-4/5}$	$\sim 1.452f^{-2/3}$

electrostatic screening, $\kappa(Ll_1)^{1/2} \rightarrow \infty$,

$$l_1 = \left(3\left(\frac{6}{\pi}\right)^{1/2}\frac{w_c lK}{\kappa^2}\right)^{2/5} L^{1/5}, \qquad \kappa(Ll_1)^{1/2} \rightarrow \infty \tag{22}$$

and for weak electrostatic screening, $\kappa \rightarrow 0$,

$$l_1 = \left(\frac{1}{15}\left(\frac{6}{\pi}\right)^{1/2} w_c lK\right)^{2/3} L, \qquad \kappa \rightarrow 0 \tag{23}$$

The dependence of l_1 on f appears through K. Substituting these results into eq 14, we get

$$\langle S^2 \rangle_b = \begin{cases} \left(\dfrac{1}{12\pi^{1/2}}\dfrac{w_c lK}{\kappa^2}\right)^{2/5} gL^{6/5}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ \left(\dfrac{1}{90\pi^{1/2}} w_c lK\right)^{2/3} gL^2, & \kappa \rightarrow 0 \end{cases} \tag{24}$$

where g and K are f-dependent as given by eqs 2 and 9. For large $f \gg 1$, eq 24 leads to

$$\langle S^2 \rangle_b = \begin{cases} \dfrac{0.792}{\pi^{1/5}}(w_c l)^{2/5}(f\kappa)^{-4/5}L^{6/5}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ \dfrac{0.085}{\pi^{1/3}}(w_c l)^{2/3}f^{-2/3}L^2, & \kappa \rightarrow 0 \end{cases} \tag{25}$$

The ratio defined in eq 20 becomes

$$g(f) = \begin{cases} 0.907gK^{2/5}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ 0.85gK^{2/3}, & \kappa \rightarrow 0 \end{cases} \tag{26}$$

and for $f \gg 1$

$$g(f) = \begin{cases} 1.942f^{-4/5}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ 1.452f^{-2/3}, & \kappa \rightarrow 0 \end{cases} \tag{27}$$

The results of eqs 26 and 27 are given in Table I for specific values of f.

The density profile inside the star polyelectrolyte can readily be obtained by the self-consistent-field theory of Edwards[16,18] or equivalently by invoking the self-similarity argument of de Gennes.[19] The monomer density $\rho(r)$ in a volume of radius r is proportional to the mass m inside this volume divided by the volume,

$$\rho(r) \sim m/r^3 \tag{28}$$

Based on self-similarity, the relation of m to r is given by eq 25 to be

$$m \sim \begin{cases} f^{2/3}\kappa^{2/3}w_c^{-1/3}r^{5/3}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ f^{1/3}w_c^{-1/3}r, & \kappa \rightarrow 0 \end{cases} \tag{29}$$

so that the density profile becomes

$$\rho(r) \sim \begin{cases} f^{2/3}\kappa^{2/3}w_c^{-1/3}r^{-4/3}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ f^{1/3}w_c^{-1/3}r^{-2}, & \kappa \rightarrow 0 \end{cases} \tag{30}$$

Table II. Dependence of the Ratio $g(p)$ of Uniform Normal Combs (with $f = 3$) on p for Different Electrostatic Screening Levels

f	good solvent ($wL^{1/2} \rightarrow \infty$)	strong screening ($\kappa(Ll_1)^{1/2} \rightarrow \infty$)	weak screening ($\kappa \rightarrow 0$)
0	1	1	1
2	0.736	0.736	0.752
3	0.704	0.704	0.729
4	0.685	0.685	0.718
5	0.673	0.673	0.713
10	0.656	0.656	0.725
15	0.657	0.657	0.744
20	0.661	0.661	0.762
25	0.666	0.666	0.776
∞	~ 0.758	~ 0.758	~ 1.0

The structure factor $S(k)$, where k is the scattering wave vector, is the Fourier transform of $\rho(r)$ in three dimensions,

$$S(k) \sim \begin{cases} f^{2/3}\kappa^{2/3}w_c^{-1/3}k^{-5/3}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ f^{1/3}w_c^{-1/3}k^{-1}, & \kappa \rightarrow 0 \end{cases} \tag{31}$$

Uniform Normal Combs

The same procedure as above can be adopted for obtaining the mean-square radius of gyration and density profile for polyelectrolytes with other branching structures. The result of eq 24 is valid except that the values of g and K are different depending on the branching architecture. As an example, for uniform normal combs with p branching units each with functionality f of 3, g is given by[2,14]

$$g = \frac{6p + 1}{(2p + 1)^2} + \frac{4p(p^2 - 1)}{(2p + 1)^3} \tag{32}$$

and the corresponding values of K are tabulated by Berry and Orofino.[14] The ratio $g(p)$ of the mean-square radius of gyration of a uniform normal comb to that of a linear chain with the same number of segments becomes

$$g(p) = \lim_{L\rightarrow\infty} \frac{\langle S^2(p) \rangle_b}{\langle S^2(p=0) \rangle_b} = \begin{cases} 0.907gK^{2/5}, & \kappa(Ll_1)^{1/2} \rightarrow 0 \\ 0.85gK^{2/3}, & \kappa \rightarrow 0 \end{cases} \tag{33}$$

The values of $g(p)$ for some values of p are given in Table II at the two extreme levels of electrostatic screening. It is to be noted that $g(p)$ goes through a minimum for intermediate values of p. The results of Table II are based on the values of g and K from Berry and Orofino.[14] For large values of p, g approaches $1/2$ and K approaches 3.61 in the case of uniform normal combs,[14] so that

$$\langle S^2 \rangle_b = \begin{cases} 0.246(w_c l)^{2/5}\kappa^{-4/5}L^{6/5}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ 0.017(w_c l)^{2/3}L^2, & \kappa \rightarrow 0 \end{cases} \tag{34}$$

$$S(k) \sim \begin{cases} \kappa^{2/3}w_c^{-1/3}k^{-5/3}, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ w_c^{-1/3}k^{-1}, & \kappa \rightarrow 0 \end{cases} \tag{35}$$

and

$$g(p) = \begin{cases} 0.758, & \kappa(Ll_1)^{1/2} \rightarrow \infty \\ 1.0, & \kappa \rightarrow 0 \end{cases} \tag{36}$$

Therefore $g(p)$ is independent of p for large p and is insensitive to the Debye screening length.

Polyelectrolyte Rings

For rings, Casassa[20] showed that g is $1/2$ and K is $\pi/2$. Substituting these values in eq 24, the mean-square radius of gyration $\langle S^2\rangle_r$ of a ring polyelectrolyte becomes

$$\langle S^2\rangle_r = \begin{cases} 0.176(w_c l)^{2/5}\kappa^{-4/5}L^{6/5}, & \kappa(Ll_1)^{1/2} \to \infty \\ 0.023(w_c l)^{2/3}L^2, & \kappa \to 0 \end{cases} \tag{37}$$

This formula recovers the limits of self-avoiding walk behavior in the fully screened situation and the circular ring behavior in the unscreened situation. The ratios g_r of the mean-square radius of gyration of a ring polyelectrolyte to that of a linear polyelectrolyte of the same molecular weight are 0.543 and 0.574 in the strong and weak screening limits, respectively.

Conclusions

A simple extrapolation formula is proposed for the mean-square radius of gyration of branched polyelectrolytes for arbitrary values of the total chain length, Debye screening length, nature of branching, number of arms in the case of regular stars, number of branch points in the case of uniform normal combs, and strength of excluded volume. The key result is the set of eqs 14–17. These formulas are general for any chemical architecture and the values of g and K appropriate to a particular type of branching are either calculated or taken as input from already existing calculations.

For uniform stars of f arms we find for strong electrostatic screening that

$$\langle S^2\rangle_b \sim (w_c lK/\kappa^2)^{2/5} gL^{6/5} \tag{38}$$

and

$$g(f) = 0.907gK^{2/5} \tag{39}$$

Although $\langle S^2\rangle_b$ depends explicitly on w_c and κ and to different extents for different values of κ, the ratio $g(f)$ is independent of w_c and κ at all levels of electrostatic screening. The same result for $g(f)$ is obtained for uniform stars in good solvents in the absence of any polyelectrolyte effect. Therefore we conclude that $g(f)$ is independent of not only the solvent quality but also the nature of any long-range interaction between segments. For large values of f, $\langle S^2\rangle_b \sim (w_c l/\kappa^2)^{2/5} f^{-4/5} L^{4/5}$, and $g(f) \sim f^{-4/5}$ in the strong screening limit. This law has been previously established for the good solution case. A different power law, $g(f) \sim f^{-2/3}$, is predicted for the weak electrostatic screening situation.

For uniform normal combs with p branching units we find the same result as eq 38 for strong electrostatic screening except that the values of g and K are different. For large values of p,

$$\langle S^2\rangle_b \sim (w_c l/\kappa^2)^{2/5} L^{6/5} \tag{40}$$

and $g(p)$ is independent of p. We also find that the mean-square radius of gyration of a ring polyelectrolyte is smaller than that of a uniform normal comb of the same molecular weight and can be smaller or larger than that of a uniform star depending on the number of arms.

For the weak electrostatic screening ($\kappa \to 0$), when the branches stretch out to become rodlike, the physically correct dependence of $\langle S^2\rangle_b$ on L is supported by the formulas presented above. Yet, the prefactors of the various formulas in this limit of $\kappa \to 0$ should be taken with caution as local chain stiffness of the chain backbone and orientational correlations of the branches, which are ignored here, are also expected to contribute to the size of the polymers. The validity of the full extrapolation formula for $\langle S^2\rangle_b$ of eq 14 with l_1 given by eqs 15–17 for arbitrary values of Debye length κ^{-1} remains to be tested.

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