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Scaling Theory of Branched Polyelectrolytes

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ABSTRACT: A scaling theory describing the equilibrium conformations of weakly charged, randomly branched polyelectrolytes in dilute and semidilute solutions is developed. We demonstrate that, in polydisperse dilute solution, small polymers are swollen by unscreened Coulomb repulsions between charged monomers while large polymers, in contrast, retain most of their counterions in the intramolecular space. As a result the intramolecular Coulomb repulsion in large polymers is partially screened. The effect of addition of salt is discussed and a power law dependence of the cluster size $\sim N^{1/2}c_s^{-1/5}$ is predicted. The concentration effects in a monodisperse salt-free solution of branched polyelectrolytes are considered. It is shown that, in the semidilute regime, the dimension of branched polyions scales as $\sim N^{1/3}$ and decreases with increasing polymer concentration because of additional screening of intramolecular Coulomb repulsion. Large clusters remain segregated (impermeable) in a wide range of the solution concentration while small clusters overlap partially.

1. Introduction

Equilibrium structural properties of solutions and melts of randomly branched polymers with short-range excluded volume interactions between monomers are presently well understood on the basis of existing theories. (see ref 1 for a review). In a pioneering work by Zimm and Stockmayer,[2] randomly branched polymers were described in the "ideal" limit, i.e., disregarding any interactions between monomers and taking into account only the branched topology of macromolecules. The account of intramolecular excluded volume interactions,[3,4] concentration effects (intermolecular interactions), and polydispersity of an ensemble of branched chains[5] on the basis of a scaling approach has provided valuable insight into the equilibrium properties of solutions and melts of branched polymers. Polydispersity effects are of special importance, because in real experimental situations, the molecular mass distribution in the reaction bath is very broad and can be described in terms of the percolation theory.

Recently, different types of water-soluble polymers became of special interest because of their technological importance driven by environmental protection reasons. Polyelectrolytes, i.e., polymers with a certain fraction of electrically charged monomers constitute one of the most important classes of water-soluble polymers.[6]

The most typical and important feature of polyelectrolytes is the long range character of the Coulomb interactions between charged monomers, which determines the equilibrium conformational properties of polyelectrolytes in solution. This Coulomb interaction is partially screened because of mobile counterions ensuring the total electroneutrality of the system. If low molecular weight salt is added to the solution, then the co- and counterions of the salt provide additional screening, and at high ionic strength, the behavior of the polyelectrolyte solution can be described in terms of short-range renormalized excluded volume interactions. In a dilute, salt-free, solution of linear weakly charged polymers, the distribution of counterions is fairly uniform. The average concentration of counterions is too small to provide screening of intramolecular Coulomb repulsions. The situation is different for weakly charged branched polyelectrolytes. As has been shown in refs 7−9 for regularly branched (star- or comb-branched) polyelectrolytes, polymers with a sufficiently large number of branches retain most of their counterions in the inner region even in the limit of strong dilution. This charge renormalization effect has been first described by Alexander et al.[10] for dilute solutions of charged colloidal particles. As a result, the intramolecular Coulomb interaction is strongly screened and the equilibrium electrostatic swelling of branches is determined by the osmotic pressure of the counterions trapped inside the star or in the region proximal to the backbone of the comb, respectively. The most typical feature of this "osmotic" regime is a virtual independence of the star (or the comb) size from the number of branches.

The first analysis of the effect of Coulomb interactions on the conformation of randomly branched polyelectrolytes has been performed in ref 11 on the basis of a Flory-type approach. Both dilute and semidilute regimes were considered, taking into account the distribution of molecular weights, which was assumed to be given by percolation, as for neutral randomly branched polymers. This implies that branched polymers were assumed to be synthesized in the neutral state with subsequent charging. However, the charge renormalization effect that we have just mentioned above was not taken into account. Because of this, the results of this analysis are valid only for small clusters. Indeed, as will be shown below, counterions may be considered as being free for small branched polymers. For sufficiently large ones, however, the attraction of counterions by the polyions becomes important. This implies that the counterions become localized within the same volume as the branched polyion: for large polyions

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charge renormalization applies. Such an effect was already studied for regularly branched polyelectrolytes in refs 7−9 and reported also for polyelectrolyte manifolds in ref 12.

The aim of the present paper is to analyze in a systematic way this charge renormalization effect for monodisperse randomly branched large clusters in both dilute and semidilute solutions: we will consider the interplay between intra- and intermolecular screening. Conformations of individual branched clusters in dilute salt-free and salt-added solutions are considered in sections 2 and 3, respectively. Section 4 deals with possible long-range ordering in salt-free dilute solutions. Cooperative screening effects in semidilute solutions are studied in section 5.

2. Dilute Solution

Following ref 11, we start our consideration with the analysis of the conformation of an individual randomly branched polymer in an infinitely dilute salt-free solution. As we shall see below, this situation, where we can neglect intermolecular interactions, corresponds to concentrations far below the overlap threshold c^*.

We utilize the classical model for the randomly branched polymer as a branched tree (without loops) formed by bi- and trifunctional monomer units. The total number of monomers is N. The branched polymers are assumed to be synthesized at a fixed value of the activity λ^2 of trifunctional monomer units. This ensures random branching. It was shown[2,13] that the average number of branching monomers is $\sim\lambda N$, so that the average number of bifunctional monomers between two successive trifunctional units is on the order of λ^{-1}. The condition $\lambda N \gg 1$ corresponds to the strongly branched limit while at low branching probability, $\lambda N \ll 1$, the linear chain behavior is recovered.

We assume that a certain fraction $\alpha \leq 1$ of monomer units bears elementary charges so that the total charge of the branched polyion is equal to $eQ = e\alpha N$. This fraction of charged monomers is set constant and independent of the local concentration of counterions. This corresponds to a large value of the ionization constant (strong electrolyte). Experimentally this system can be realized in three steps: (i) polymerization of a mixture of neutral bi- and trifunctional monomers, (ii) chemical modification of a certain fraction of monomers resulting in the appearance of ionizable functional groups on the chains (for example, sulfonation of styrene monomers), and (iii) dilution in a polar solvent, e.g., in water, which results in dissociation of ionizable groups and appearance of charges in the chain.

The strength of electrostatic interactions in the system is characterized by the Bjerrum length, $l_{\mathrm{B}} = e^2/\epsilon k_{\mathrm{B}}T$, where ϵ is the dielectric constant of the solvent, and the monomer length a is assumed to be of the same order as l_{B}. We assume the condition of weak charging, $\alpha \ll (l_{\mathrm{B}}/a)^2 \sim 1$ to be fulfilled. The latter implies that the chain part between two neighboring charged monomers retains Gaussian statistics unperturbed by the Coulomb repulsions.

Only the electrostatic interactions between charged monomers and counterions are taken into account in our system. In other words, we neglect excluded volume interactions between noncharged monomers: for $\alpha = 0$, when the polymer is not charged, the ideal branched polymer behavior is recovered.

This approximation may be supported by the following arguments:

(i) In the main regimes of interest, it is the Coulomb interaction that determines the conformation of the branched polyelectrolyte. Excluded volume interactions might slightly modify the local conformational structure of the extended branches but do not change it dramatically.

(ii) In many cases water is a marginally good or even a poor solvent for uncharged monomers and only charges provide the solubility of a branched polyion as a whole in water. In this case, excluded volume repulsion of noncharged monomers is partially compensated by binary attraction; i.e., the solvent is close to the Θ-conditions for linear chains. Of course, the ternary repulsive interactions which can induce swelling of branched polymers in a Θ-solvent remain, but they can be neglected in the regimes of predominance of Coulomb repulsion, and the elasticity of linear fragments of the branched polymer must be Gaussian.

2.1. Small (Unscreened) Clusters. The equilibrium swelling of a branched polyelectrolyte in a dilute salt-free solution is determined by the balance of Coulomb repulsions between charged monomers and the conformational entropy losses because of the extension of all the branches. Within a Flory approximation the free energy of a uniformly swollen cluster can be written as

$$F/k_{\mathrm{B}}T \cong \frac{R^2}{(N/\lambda)^{1/2}a^2} + \frac{l_{\mathrm{B}}(\alpha N)^2}{R} \tag{1}$$

where the first term describes the conformational (elastic) contribution[4], $R_{\mathrm{g}}(N) \cong (N/\lambda)^{1/4}a$ is the unperturbed (Gaussian) size of an ideal branched polymer.[2] The second term accounts for the Coulomb repulsions between charged monomers in the unscreened limit: all the counterions are supposed to leave the inner region of the branched polyion and to spread uniformly in the large volume of the solution. As we shall see below, this approximation is valid only for sufficiently small clusters and fails for large ones. Minimization of the free energy, eq 1, with respect to the dimension R of a polymer gives us the equilibrium size of a branched polyelectrolyte as a function of molecular weight N, and degree of ionization α

$$R_{\mathrm{N}} \cong N^{5/6}a\alpha^{2/3}(l_{\mathrm{B}}/a)^{1/3}\lambda^{-1/6} \tag{2}$$

The latter equation was already obtained earlier in ref 11, and as we shall demonstrate below, its range of validity is restricted from both small and large values of N. It is instructive to mention also that in the limit $\lambda \cong N^{-1}$ eq 2 crosses over to the result $R_{\mathrm{N}} \cong Na\alpha^{2/3}(l_{\mathrm{B}}/a)^{1/3}$, for the size of a linear chain polyelectrolyte in a dilute solution.[14,15]

Equation 2 shows that the intramolecular Coulomb repulsion is strong enough to perturb the conformation of branched polymer if the number of monomers in a cluster is sufficiently large. More explicitely, this is the case if $N \gg \tilde{N} \cong \alpha^{-8/7}(l_{\mathrm{B}}/a)^{-4/7}\lambda^{-1/7}$, i.e., $R_{\mathrm{N}} \gg \tilde{R} \cong \alpha^{-2/7}(l_{\mathrm{B}}/a)^{-1/7}\lambda^{-2/7}a$. The clusters of smaller size, $N \ll \tilde{N}$, retain their Gaussian dimensions, $R_{\mathrm{g}}(N) \cong (N/\lambda)^{1/4}a$.

In the case of $N \gg \tilde{N}$, when the branched chain as a whole is swollen by the Coulomb repulsions, it is instructive to distinguish two cases:

(i) If $\tilde{N} \ll \lambda^{-1}$, that is for $\alpha \gg \lambda^{3/4}(l_{\mathrm{B}}/a)^{-1/2}$, then every linear fragment of the polymer between two neighboring branching point (the average number of monomers in this fragment is $\sim\lambda^{-1}$) is extended by the Coulomb repulsion of its charged monomers. We remark that the latter condition coincides with the condition of extension of a linear polyelectrolyte chain consisting of $n \cong \lambda^{-1}$ monomers with respect to its Gaussian size, $n\alpha^{2/3}\cdot(l_B/a)^{1/3}a \gg n^{1/2}a$. Hence, every linear fragment between branching points is stretched up to a size $r_n \cong \lambda^{-1}\cdot\alpha^{2/3}(l_B/a)^{1/3}a$ and the overall branched chain size may be written as

$$R \cong (N/n)^{5/6} r_n \tag{3}$$

(ii) If $\tilde{N} \gg \lambda^{-1}$, when the fraction of charged monomers is sufficiently small, $\alpha \ll \lambda^{3/4}(l_B/a)^{-1/2}$, the Coulomb repulsions are not strong enough to stretch linear sequences between branching points. These sequences retain Gaussian dimension, $r_n \cong n^{1/2}a$. For small scales, for parts of the polymer smaller than $\tilde{N}$, the branched polymer retains ideal (Gaussian) statistics while for larger distances its structure is determined by the Coulomb repulsions:

$$R_N \cong (N/\tilde{N})^{5/6} R_g(\tilde{N}) \tag{4}$$

where $R_g(\tilde{N}) \cong (\tilde{N}/\lambda)^{1/4}a$.

2.2. Large (Screened) Clusters. As we have already noted, the range of validity of eq 2 is restricted not only from below, $N \gg \tilde{N}$, but from above as well.

As follows from eq 2, the cluster size grows with increasing N, but not as fast as the overall charge of the branched polyion $Q \sim N$. As a result, for large clusters, the approximation of free counterions is not valid anymore and charge renormalization occurs.

The effect of charge renormalization was originally discussed for charged colloidal particles in dilute salt-free solution by Alexander et al. in ref 10. The physical origin of the effect is the following: we look for a solution of the nonlinearized Poisson–Boltzmann equation for a system consisting of immobilized charges eQ located in a finite region ω of 3-dimensional space and of an ensemble of mobile counterions confined in a volume Ω ($\omega \in \Omega$). In the limit of $\omega \ll \Omega$ corresponding to the conditions of dilute solution the distribution of counterions depends crucially on the ratio between the value of the immobilized charge, Q, and the dimension of the localization region $R \sim \omega^{1/3}$. At $Q \ll (R/l_B)\ln(\Omega/\omega)$, the counterions are essentially free and are distributed more or less uniformly in the whole available space Ω. In the opposite limit, for $Q \gg (R/l_B)\ln(\Omega/\omega)$, the Coulomb attraction of the counterions by the immobilized charges is strong enough to retain most of counterions in the region ω where the immobilized charge is localized so that the total, uncompensated, charge inside the region ω is $\sim R/l_B$. The onset of charge renormalization corresponds to a value of the immobilized charge $Q \cong R/l_B \ln(\Omega/\omega)$, and an additional increase in Q does not lead (with the accuracy of weak logarithmic terms) to an increase in the overall charge within ω. This result can be easily rationalized by comparing the energy $\sim e^2Q/\epsilon R$ of the Coulomb attraction retaining the counterion in the region ω with the thermal energy k_BT (within the accuracy of a factor $\sim\ln(\Omega/\omega)$. The latter described the gain in the translational entropy of a counterion released from ω into the region Ω.)

Hence, we expect that, even in a dilute solution, sufficiently large branched polyelectrolytes retain most of their counterions inside. These counterions almost compensate the bare charge of the polyion so that the actual charge within the branched polyion is much smaller than its bare charge $eQ = e\alpha N$. The onset of charge renormalization determines the crossover value N^* between "small" and "large" clusters. Within logarithmic corrections which are omitted in our scaling analysis, it can be determined from the condition $\alpha N^* \cong R(N^*)l_B^{-1}$ where $R(N^*)$ is given by eq 2. The result

$$N^* \cong \alpha^{-2}\lambda^{-1}(l_B/a)^{-4}, \tag{5}$$

shows that unscreened clusters can be found in the solution only if the fraction α of charged monomers is sufficiently small.

The equilibrium swelling of large polymers, $N \gg N^*$, is determined primarily not by Coulomb repulsions between charged monomers, which are screened by counterions, but by the osmotic pressure of the counterions trapped inside the volume occupied by branched chain. The two competing contributions to the free energy of the branched chain can be written as

$$F/k_BT \cong \frac{R^2}{N^{1/2}\lambda^{-1/2}a^2} - \alpha N \ln R \tag{6}$$

where the last term accounts for the translational entropy of trapped counterions. We remind the reader that as long as we consider branched polyelectrolytes comprising weakly charged linear segments, the correlations in positions of charged monomers and counterions inside the clusters can be neglected. Then the translational entropy of trapped counterions provied the dominant contribution to the free energy of the cluster, as expressed by eq 6. Minimization of the free energy, eq 6 leads to

$$R_N \cong N^{3/4}\alpha^{1/2}\lambda^{-1/4}a \tag{7}$$

Hence, we find that, for large ($N \gg N^*$) branched polyelectrolytes, an "osmotic" regime, characterized by the localization of most of counterions inside the volume of the chain even in dilute solution, takes place. Similar regimes characterized by the localization of counterions were found earlier for planar polyelectrolyte brushes[7,16] and star- and comb-branched polyelectrolytes[8,9] in dilute salt-free solutions. As the swelling of the polyelectrolytes in this regime is determined by the osmotic pressure of counterions, the equilibrium size becomes *independent* of the strength of the Coulomb interaction characterized by l_B.

The crossover between unscreened (barely charged) and screened (osmotic) regimes occurs for $N \cong N^*$ or $R_{N^*} \cong l_B\alpha N^*$.

Because of the "trapping" of most of the counterions inside the large polymers, the renormalized (uncompensated) charge of a large ($N \gg N^*$) cluster is equal to

$$\tilde{Q} \cong R_N/l_B \cong N^{3/4}\alpha^{1/2}\lambda^{-3/4}(l_B/a)^{-1} \tag{8}$$

where R_N is given by eq 7. This is much smaller than the overall bare charge Q of the cluster,

$$\tilde{Q}/Q \cong (N/N^*)^{-1/4} \tag{9}$$

The counterions trapped inside the cluster provide a screening of the Coulomb interactions between charged monomers. The corresponding Debye screening length can be estimated as

$$r_D(N) \cong (l_B c_i(N))^{-1/2} \tag{10}$$

where

$$c_i(N) \cong (Q - \tilde{Q})/R_N^{\ 3} \cong Q/R_N^{\ 3} \tag{11}$$

is the concentration of trapped counterions inside the cluster. Hence, for large polymers which are in the osmotic regime, we find

$$R_N/r_D(N) \cong (N/N^*)^{1/8} \gg 1,\ N \gg N^* \tag{12}$$

Thus, the "internal" screening length, $r_D(N)$, is much smaller than the overall size of the polymer. This implies that the local electroneutrality condition holds inside the osmotic cluster for distances larger than $r_D(N)$, while the parts of the cluster smaller than $r_D(N)$ remain unscreened. In other words we can subdivide the large osmotic cluster into subclusters of size $r_D(N)$. Each clusters is made of g_D monomers, where g_D can be determined from the condition

$$r_D(N) \cong g_D^{\ 5/6}\alpha^{2/3}(l_B/a)^{1/3}\lambda^{-1/6}a \tag{13}$$

The relation between $r_D(N)$ and g_D is the same as the one between the size and the number of monomers in unscreened branched polyelectrolyte, eq 2. As the parts of branched polyelectrolyte of size $r_D(N)$, or larger, are electroneutral, the overall size of the osmotic cluster can be considered as the size of a neutral branched polymer[3,4] consisting of N/g_D neutral impermeable "superblobs" of size $r_D(N)$

$$R_N \cong (N/g_D)^{1/2}r_D(N) \tag{14}$$

that coincides with eq 7.

We note that the size of a branched polyelectrolyte in the osmotic regime, eq 7, (for $N \gg N^*$) can also be obtained as the size of a neutral branched polymer with excluded volume interactions, $R_N \cong N^{1/2}\lambda^{-1/10}(v_{DH}a^{-3})^{1/5}a$. Here, the renormalized excluded volume parameter (second virial coefficient of the monomer−monomer interaction), v_{DH}, is determined by the screened Coulomb (Debye−Hückel) repulsion between charged monomers:

$$v_{DH} \cong \alpha^2 l_B r_D^{\ 2} \tag{15}$$

where the factor α^2 appears because only a fraction α of monomers is charged.

3. Effect of the Addition of Salt

Addition of a low molecular weight salt in the solution induces (additional) screening of intramolecular Coulomb repulsions and, as a result, deswelling of branched polyelectrolytes. As we demonstrate below, the effect of added salt is also different for large and small branched polyions.

We start our discussion with the case of large clusters, $N \gg N^*$, where the intramolecular Coulomb repulsion is already strongly screened by counterions in a salt-free solution. We expect that the addition of salt affects only weakly the conformation of large clusters as long as the salt concentration remains smaller than the concentration c_i of counterions in the intramolecular space. An equivalent condition is that the intrinsic screening length $r_D(N)$ remains smaller than the screening length in the bulk of the solution, $r_D(c_s) \cong (l_B c_s)^{-1/2}$. The onset c^*_s of the salt-induced deswelling of a branched cluster can be determined from the condition $r_D(c^*_s) \cong r_D(N)$. This leads to

$$c^*_s \cong N^{-4/5}\alpha^{-1/2}\lambda^{3/4}a^{-3},\ N \gg N^* \tag{16}$$

At salt concentrations above c^*_s the branched polyelectrolyte retains the structure of an unscreened cluster in a salt-free solution for distances smaller than $r_D(c_s)$. When the Coulomb repulsion is screened on distances larger than $r_D(c_s)$, the branched polyelectrolyte as a whole can be presented as a cluster consisting of neutral superblobs of size $r_D(c_s)$,

$$R_N(c_s) \cong (N/g_D(c_s))^{1/2}r_D(c_s) \tag{17}$$

where the number of monomers in the superblob is determined by the salt concentration:

$$r_D(c_s) \cong g_D^{\ 5/6}(c_s)\alpha^{2/3}(l_B/a)^{1/3}\lambda^{-1/6}a \tag{18}$$

Hence, the size of the branched polyelectrolyte decreases with increasing salt concentration as $R_N(c_s) \sim c_s^{-1/5}$. The same result can be obtained if we describe a branched cluster in the regime of salt-dominated screening as a neutral polymer with an effective excluded volume parameter $v_{DH} \cong l_B\alpha^2 r_D^2(c_s)$. Obviously eqs 17 and 7 merge for $c_s \cong c^*_s$.

The picture of a salt-induced deswelling of a branched polyelectrolyte as well as eq 17 for its size remains valid also for small clusters, $N \ll N^*$. However, in the latter case, the effect of salt becomes important when the salt-controlled Debye length $r_D(c_s)$ becomes comparable with the overall size of a cluster R_N. This gives another estimate for c^*_s

$$c^*_s \cong N^{-5/3}\alpha^{-4/3}\lambda^{1/3}(l_B/a)^{-5/3}a^{-3},\ N \ll N^* \tag{19}$$

It may be seen from eqs 16 and 19 that the onset of salt-induced deswelling of a branched cluster is displaced to lower salt concentrations with increasing N. This effect is more pronounced for small, originally unscreened, clusters and becomes weaker for large clusters which are characterized by a finite intrinsic screening length even in the dilute limit.

4. Dilute Solutions: Screening and Long-Range Order

In this section, we start to analyze the concentration effects in salt-free solutions of randomly branched polyelectrolytes, assuming that all branched polyions have the same molecular weight (monodisperse case).

Let c be the concentration of *monomers*. The concentration of polyions is equal to c/N. Then the *average* concentration of counterions ensuring screening of Coulomb interactions in the solution is equal to αc. However, as we know from the previous section, the distribution of counterions in the solution depends strongly on the number of monomers N per branched polyion.

If $N \ll N^*$, then as a first approximation we can assume that all the counterions are free to move and are distributed almost homogeneously in the whole available volume of the solution. As a result, at small concentrations, barely charged polyions are immersed in a "homogeneous sea" of counterions with a concentration αc providing the screening of Coulomb interactions for distances larger than $\bar{r}_D(c) \cong (l_B c)^{-1/2}$. Note that we use here $\bar{r}_D$ in order to distinguish the "average" from the "internal" screening length $r_D(N)$. These are different for large polyions; see below.

Of course at any finite concentration of polyelectrolytes, the counterions are distributed in the solution inhomogeneously: their local concentration is larger in the vicinity of the polyions. However, in our scaling approach we can take into account this nonlinear screening effecs only by distinguishing the cases of "small", $N \ll N^*$, and "large", $N \gg N^*$, branched polyions. The approximation of uniform counterions distribution is applicable in the former case, while in the latter case the distribution of counterions in dilute solution is essentially inhomogeneous. As most of counterions are "trapped" inside large clusters by Coulomb attraction, their concentration inside these clusters is approximately equal to $\alpha N/R_N^3$, where R_N is the size given by eq 7 in the strong screening limit. At the same time the counterions concentration in the space between polyions is much smaller and is determined by the small fraction of counterions released by polyions into the solution, so that it is given by

$$\tilde{c}_i \cong \frac{\tilde{Q}c}{N} \cong \frac{R_N}{l_B}\frac{c}{N} \tag{20}$$

Correspondingly, the Debye length $\tilde{r}_D(c)$ responsible for the screening of Coulomb repulsions *between* clusters in the solution is much larger than the "internal" Debye length inside clusters defined by eq 10.

Because of the long-range character of Coulomb interactions between branched polyions, one can expect that even in dilute salt-free solutions at concentrations far below the overlap concentration they can form a periodic lattice. This is analogous to colloidal crystals formed by charged colloidal particles.[10] The long-range order in this periodic lattice is stabilized by the energy of Coulomb repulsions between polyions when it becomes larger than k_BT. Hence, the condition of stability of the colloidal crystal can be determined as

$$l_B \tilde{Q}^2 \left(\frac{c}{N}\right)^{1/3} \geq 1 \tag{21}$$

where $\tilde{Q}$ is the effective (uncompensated) charge of a branched polyion: $\tilde{Q} \cong Q$ for small, unscreened clusters and $\tilde{Q} \cong R_N/l_B \ll Q$ for large, screened ones. $(N/c)^{1/3}$ is the average distance between polyions in the solution. Hence, because of the difference in the distribution of counterions in solutions of small and large clusters, we obtain different scaling dependences for the concentration c_{crist} corresponding to the colloidal crystallization threshold:

$$c_{\text{crist}} \cong \begin{cases} N^{-5}\alpha^{-6} l_B^{-5} & N \ll N^* \\ N^{-7/2}\alpha^{-3}\lambda^{3/2}(l_B/a)^3 a^{-3} & N \gg N^* \end{cases} \tag{22}$$

As expected, c_{crist}, decreases with increasing N, or, equivalently, with increasing charge of branched polyion. But the slope $-\, d \ln c_{\text{crist}}/d \ln N$ is smaller for large N than for small N because of the partial compensation of the charge of a polyion by trapped counterions.

When concentration increases above the crystallization threshold, $c \gg c_{\text{crist}}$, the average distance between branched polyions decreases. However, the Coulomb repulsion, which provides long-range order in the array of branched polyions, is simultaneously screened more strongly. Because of this screening, the colloidal crystal melts at high concentration, for $c \gg c_{\text{melt}}$. The condition for melting, $\bar{r}_D(c) \ll (c/N)^{-1/3}$, or $\tilde{r}_D(c) \ll (c/N)^{-1/3}$ (in the $N \gg N^*$ case), gives us an estimate for c_{melt} as

$$c_{\text{melt}} \cong \begin{cases} N^{-2}\alpha^{-3} l_B^{-3} & N \ll N^* \\ N^{-5/4}\alpha^{-3/2}\lambda^{3/4} a^{-3} & N \gg N^* \end{cases} \tag{23}$$

It is remarkable that because of the small concentration of counterions in the intercluster space in the case of large clusters, the colloidal order remains until the geometrical overlap concentration, $c_{\text{melt}} \cong N/R_N^3 \equiv c_{\text{overlap}}$. Hence, the accumulation of counterions inside large clusters and the corresponding strongly reduced concentration of counterions in the inter-polyion space lead to a shift to larger concentrations of the range of stability of colloidal crystal formed by branched polyelectrolytes. As we discuss below, the liquidlike short-range order in solutions of strongly branched polyelectrolytes remains even at concentrations above c_{overlap}.

5. Semidilute Solution: Screening of Coulomb Interactions

The crossover between the dilute and semidilute regimes of monodisperse solutions of randomly branched polyelectrolytes occurs in different ways depending on the cluster sizes, i.e., on the ratio between N and N^*.

5.1. Small Clusters, $N \ll N^*$. In this case, as a first-order approximation, we can assume the uniform distribution of counterions and neglect nonlinear screening effects. The Debye screening length at all concentrations is determined by the average concentration of counterions in the solution and is equal to $\bar{r}_D \cong (l_B \alpha c)^{-1/2}$.

It seems reasonable to define the crossover concentration c^* from dilute to semidilute regimes from the condition

$$(R_N/\bar{r}_D)_{c = c^*} \cong 1 \tag{24}$$

where R_N is the size of the cluster in dilute solution, as given by eq 2. Equation 24 implies that at $c \ll c^*$ branched polyions retain the same conformation as in dilute solution while in the opposite limit, $c \gg c^*$, the collective (screening) effects become important. Using eq 2 we obtain

$$c^* \cong N^{-5/3}\alpha^{-7/3}(l_B/a)^{-5/3}\lambda^{1/3}a^{-3} \tag{25}$$

We note that in the linear polymer limit, $\lambda \cong N^{-1}$, the same type of arguments lead[17] to a crossover concentration between dilute and semidilute regimes, $c^* \cong N^{-2}\alpha^{-7/3}(l_B/a)^{-5/3}a^{-3}$ and to the following concentration dependence of the chain size in a semidilute solution

$$R(c) \cong N^{1/2}\alpha^{1/12}(l_B/a)^{-1/12}(ca^3)^{-1/4}a \tag{26}$$

The latter equation can be obtained by applying scaling arguments and imposing the requirement that $R \sim N^{1/2}$, corresponding to the screening of long-range intermolecular interactions in semidilute solution.

An increase of the solution concentration above c^* must result in a gradual collapse of the branched polyions because of the screening of the Coulomb repulsive interactions between charged monomers. To derive the concentration dependence of the cluster size $R_N(c)$ in the range $c \gg c^*$, we can assume the following scaling arguments

$$R_N(c) \cong R_N|_{c=0}\left(\frac{c}{c^*}\right)^x \tag{27}$$

where the exponent x is to be specified. We expect that for $c \gg c^*$, when the Coulomb interactions are screened for distances smaller than the size of a cluster, the exponent for the molecular weight dependence of the cluster size must be the same as for semidilute solutions and melts of neutral branched polymer;[4] i.e., $R_N(c) \sim N^{1/3}$. This implies a value of the exponent $x = {}^3/_{10}$, so that the cluster size varies as

$$R_N(c) \cong N^{1/3}\alpha^{-1/30}(l_B/a)^{-1/6}\lambda^{-1/15}(ca^3)^{-3/10}a \tag{28}$$

Note that similar scaling arguments may be applied to the correlation length $\xi(c)$. Combined with the requirement that $\xi(c) \sim N^0$ at $c \gg c^*$, they lead to $\xi(c) \cong (l_B\alpha c)^{-1/2} \equiv \bar{r}_D$. We remark that a similar expression for the size of the cluster, eq 28, can be obtained as

$$R_N(c) \cong \left(\frac{N}{\bar{g}_D}\right)^{1/3}\bar{r}_D \tag{29}$$

where the number of monomer $\bar{g}_D$ in the concentration branched blob of size $\bar{r}_D$ is determined by

$$\bar{r}_D \cong \bar{g}_D^{\,5/6}\alpha^{2/3}(l_B/a)^{1/3}\lambda^{-1/6}a \tag{30}$$

i.e., by the same relation which holds for unscreened clusters in the dilute regime, eq 2. Hence, for distances smaller than a screening length $\bar{r}_D$ determined by the solution concentration, the clusters retain the same structure as in a dilute regime while for larger distances the branched blobs of size $\bar{r}_D$ make a compact structure with a size given by eq 28.

It is important to note that according to eq 28 the degree of overlapping of branched clusters increases with increasing concentration c above c^*.

Equation 28 holds until the number of monomers $\bar{g}_D$ per branched concentration blob becomes larger than $n \equiv \lambda^{-1}$, i.e., until the concentration blob contains many linear subchains. The crossover $\bar{g}_D \cong n$ occurs at $c \cong c^{**} \cong \alpha^{-7/3}(l_B/a)^{-5/3}\lambda^2a^{-3}$ Note that $c^{**}/c^* \cong (\lambda N)^{5/3} \gg 1$ for strongly branched polyelectrolytes.

One can easily check that eq 28 is valid for $c^* \ll c \ll c^{**}$ and gives an intramolecular density of monomers of the polyion, $N/R_N^3(c)$, smaller than the average overall density, c. This corresponds to the overlapping of clusters in this concentration range.

For $c \gg c^{**}$, each linear subchain between branching points behaves as an individual linear chain in a semidilute polyelectrolyte solution of concentration c. Because of electrostatic screening, its size varies as

$$r_n(c) \cong n^{1/2}\alpha^{1/12}(l_B/a)^{-1/12}(ca^3)^{-1/4}a \tag{31}$$

to be compared with eq 26. The overall size of the cluster is given by

$$R_N(c) \cong \left(\frac{N}{n}\right)^{1/3}r_n(c) \cong N^{1/3}\alpha^{1/12}(a/l_B)^{1/12}\lambda^{-1/6}(ca^3)^{-1/4}a \tag{32}$$

Thus, the linear chain exponent $-{}^1/_4$ for the concentration dependence of the branched polyelectrolyte size is recovered. Further increase in the concentration of the solution and strengthening of screening results in the shrinking of every linear subchain and of the branched cluster as a whole, eq 32, until the subchains reach their Gaussian size, $r_n \cong n^{1/2}a$ and the cluster as a whole acquires a size

$$R_N(c) \cong N^{1/3}n^{1/6}a \tag{33}$$

This happens at a concentration $c \cong (\alpha a/l_B)^{1/3}a^{-3}$. We note that the latter concentration is larger than c^{**} only for sufficiently large degree of ionization, $\alpha \gg \lambda^{3/4}(l_B/a)^{-1/2}$. This ensures the stretching of each linear subchain by unscreened Coulomb repulsions in the dilute regime. When this is not the case, the $c^{-1/4}$ regime of the collapse of the branched cluster induced by the increase in the concentration does not occur.

5.2. Large Clusters, $N \gg N^*$. As we have discussed in section 2, large clusters retain most of their counterions in the intracluster region even in a dilute solution. As a result, the distribution of counterions in a dilute solution is essentially inhomogeneous: in the intraclusters space the concentration of counterions is sufficiently large, $\alpha N/R_N^3$, and is virtually independent of the solution concentration c. In the intercluster space, it is determined by the small fraction of counterions released by the clusters in the bulk of the solution and is given by $\tilde{c}_i \cong R_Nc/Nl_B$. Hence, we can introduce two different screening lengths, $r_D(N) \cong (l_Bc_i(N))^{-1/2}$ and $\tilde{r}_D(c) \cong (l_B\tilde{c}_i)^{-1/2}$ which determine screening of intra- and intermolecular Coulomb interactions, respectively. Obviously $c_i(N) \gg \tilde{c}_i$ and $r_D(N) \ll \tilde{r}_D(c)$ if $N \gg N^*$.

Consequently, the crossover concentration c^* between dilute and semidilute regimes coincides with the overlap concentration

$$c^* \cong c_{\text{overlap}} \cong N/R_N^{\ 3},\ N \gg N^* \tag{34}$$

where R_N is determined by eq 7. Note that for $N \cong N^*$ both definitions of c^* for small and large clusters coincide.

At $c \cong c^*$, the crossover $\tilde{r}_D(c) \cong r_D(N)$ occurs. For $c \gg c^*$, there is only one screening length, $\bar{r}_D(c) \cong (l_B\alpha c)^{-1/2}$.

Applying the same scaling arguments as in section 5.1 and using eq 34 for c^* we find, that the size of the clusters in the semidilute regime scales as

$$R_N(c) \cong (N/c)^{1/3} \tag{35}$$

As concentration is increased above c^*, the clusters remain closely packed and do not penetrate each other. The solution as a whole can be described as a system of close-packed clusters of size given by eq 35, while each cluster consists of close-packed subclusters (branched concentration blobs) of size ξ_c

$$R_N(c) \cong \left(\frac{N}{g_c}\right)^{1/3}\xi_c \tag{36}$$

The intrinsic structure of these blobs remains unperturbed by concentration effects. It coincides with that of the “osmotic cluster” in the dilute regime:

$$\xi_c \cong g_c^{3/4} \alpha^{1/2} \lambda^{-1/4} a \tag{37}$$

(see eq 7). To determine the size ξ_c of a concentration blob, we apply the following scaling argument

$$\xi_c \cong R_N(c)|_{c=0}(c/c^*)^y \sim N^0 \tag{38}$$

which gives the exponent $y = {}^3/_5$ and

$$\xi_c \cong \alpha^{-2/5} \lambda^{1/5} (ca^3)^{-3/5} a \tag{39}$$

The latter expression for the size of the concentration blob can be obtained from the equation for the concentration blob size in a semidilute solution of neutral branched polymers under good solvent conditions[4] if we substitute the monomer−monomer excluded volume v by the second virial coefficient of the monomer−monomer interaction via screened Coulomb potential v_{DH}, eq 15. Equation 39 implies that the size of the concentration blob ξ_c decreases with increasing c faster than the screening length $\bar{r}_D(c) \sim c^{-1/2}$. As a result, the nonpenetration regime described above occurs only in the concentration range $c^* \ll c \ll c^{***}$where $c^{***} \cong \alpha\lambda^2 l_B{}^5 a^{-8}$ is defined from the crossover condition $\xi_c(c^{***}) \cong \bar{r}_D(c^{***})$.

The concentration c^{***} corresponds to the upper boundary of the noninterpenetrating regime. For concentrations $c \gg c^{***}$, partial interpenetration of clusters occurs and eqs 28−33 hold. Thus, the difference in the behaviors of large ($N \gg N^*$) and small ($N \ll N^*$) clusters disappears.

6. Discussion and Conclusions

We used scaling arguments to analyze the equilibrium structure and screening effects in dilute and semidilute solutions of randomly branched, weakly charged polyelectrolytes. The most important conclusion is that in dilute solution of large branched clusters the distribution of counterions is essentially inhomogeneous: the counterions are localized predominantly in the intramolecular space ensuring partial screening of intramolecular Coulomb repulsion. As a result, the molecular weight dependence of the cluster dimension is different for small, unscreened branched clusters and for large, screened ones (see Figure 1). This can be interpreted also in terms of the variable fractal dimension of charged randomly branched clusters: the latter is found to be smaller for unscreened clusters than for screened ones. With increasing concentration of the solution, we expect the appearance of an ordered array of charged clusters similar to those found in solutions of charged colloidal particles. For large clusters, this order is retained up to the geometrical overlap concentration because of low concentration of counterions in the intermolecular space. As a result, comparatively weak screening of intramolecular Coulomb repulsions ensures long-range order in the system. These theoretical predictions are in good agreement with the recent experimental data of Guenoun et al.[18] obtained by small-angle neutron scattering in dilute salt-free solutions of micelles, formed by end-hydrophobically modified polyelectrolytes (PSSNa). Because of the high stability of the aggregation number as a function of the polymer and/or salt concentration and small core size, these micelles well mimic star-branched polyelectrolytes. The appearance of the peak in the scattering intensity at the wave vector q^* corresponding to the average intermicellar distance in the range of dilute solutions indicates the presence of long-range order in the array of charged micelles. This peak is observed in a wide range of concentrations both below and even above (in the case of weakly branched micelles) the overlap concentration. The topology of many-chain spherical micelles is different from randomly branched clusters considered in our paper. However, the major trend consisting in the possibility of stabilization of colloidal long-range crystalline order by Coulomb repulsions between highly branched polyelectrolytes in salt-free solutions is clearly supported by these experiments. For concentrations above the overlap concentration, in the semidilute regime, we predict that large clusters do not penetrate each other in a wide concentration range, while small clusters interpenetrate partially. This is reflected by different concentration dependences of the large and small cluster sizes in the semidilute regime.

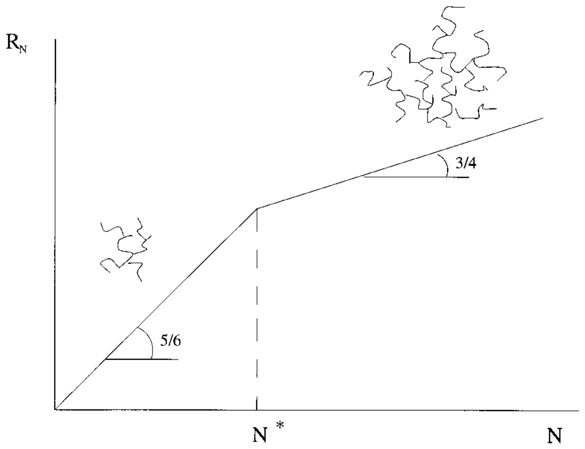

Figure 1. Schematic dependence of the branched polyelectrolyte size, R_N, on the degree of polymerization, N, in log−log coordinates. The ranges of small $N \ll N^*$(unscreened) and large $N \gg N^*$ (osmotic) clusters are depicted.

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Glossary

a	the monomer length
c	concentration of the monomer units, in particular:
c_{crist}	corresponding to the onset of colloidal crystallization
c_{melt}	corresponding to the melting of the colloidal crystall
c^*	corresponding to the crossover between dilute and semidilute solutions
c^{**}	at which the number of monomers $\bar{g}_D$ per superblob of size $\bar{r}_D$ is equal to n
c^{***}	at which $\xi_c = \bar{r}_D(c)$
c_s	salt concentration in the bulk of the solution, in particular:
$c^*{}_s$	corresponding to the onset of the salt-induced deswelling
$c_i(N)$	intrinsic concentration of counterions in large, $N \gg N^*$, clusters
$\tilde{c}_i$	concentration of counterions in the intercluster space

g_D	number of monomers in a superblob of size $r_D(c_s)$ (salt-added solution)
$\bar{g}_D$	number of monomers in a superblob of size $\bar{r}_D$ (semidilute salt-free solution)
k_B	Boltzmann constant
l_B	Bjerrum length
N	number of monomers in a branched polyelectrolyte, in particular:
N^*	corresponding to the onset of charge renormalization
$\tilde{N}$	corresponding to the onset of the electrostatic swelling (in a salt-free solution)
$n \cong \lambda^{-1}$	average number of monomers between branching points
Q	the bare charge of a branched polyelectrolyte
$\tilde{Q}$	uncompensated charge inside the branched polyelectrolyte
$R_g(N)$	Gaussian size of a randomly branched (neutral) polymer
R_N	size of a branched polyelectrolyte in a dilute salt-free solution
$R_N(c)$	the same in a semidilute solution of concentration c
$R_N(c_s)$	the same in a dilute salt-added solution
$r_D(c_s)$	bulk Debye screening length
$r_D(N)$	intrinsic screening length inside large, $N \gg N^*$, clusters
$\bar{r}_D \equiv \bar{r}_D(c) \cong (l_B \alpha c)^{-1/2}$	screening length in a semidilute solution (quasi-uniform distribution of counterions)
$\tilde{r}_D(c) \cong (l_B \alpha \tilde{c})^{-1/2}$	screening length in the intercluster space
r_n	size of a linear segment between the branching points
α	a fraction of charged monomers
λ^2	activity of trifunctional monomer units
ξ_c	correlation length in a semidilute solution

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