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Conformations of Star-Branched Polyelectrolytes

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Abstract. — Scaling theory describing the conformations of weakly charged star-branched polyelectrolytes in dilute and semi-dilute salt-free solutions is developed. The dependence of the star size on the number of branches as well as on the solution concentration is analyzed. It is shown that the star size increases with an increase in the number of branches, f , at small f and tends to a constant value at large f . An increase in the concentration of stars in a solution results in a decrease in the star size R according to the power law: $R \sim c^{-1/3}$ in the range of a moderate concentration and $R \sim c^{-1/4}$ at larger concentration. For stars with a small number of branches the behavior $R \sim c^{-1/2}$ in a certain concentration range is also predicted. The collapse transition which occurs in the polyelectrolyte star if the solvent strength decreases is considered; it is shown that the collapse of a polyelectrolyte star may be accompanied by the loss of the star spherical symmetry.

1. Introduction

The interest to the equilibrium and dynamic properties of the solutions of polymers with complex architecture, in particular to the solutions of branched polymers on the one hand, and to polyelectrolytes on the other hand has noticeably increased during the last years. The combination of chemical and topological complexity as well as different types of interactions (short- and long-range interactions) provide new specific features of static and dynamic behavior of these systems and makes them interesting for different applications.

A certain level of understanding of the equilibrium properties of solutions of uncharged regularly branched (star-branched, comb-like polymers) has been achieved [1–6] on the basis of scaling concept. The predictions of these scaling theories have been well confirmed by experimental data [7, 8] and simulation results [9, 10].

The stretching of linear fragments (star arms, side and main chains of combs) of branched polymers with respect to the dimensions of equivalent linear chains in a solution of the same concentration is the typical feature of branched polymers behavior. This stretching results from intramolecular repulsive interactions which are sufficiently strong due to branched topology (large intramolecular monomer density) and becomes stronger as the degree of branching increases. The stretching is most pronounced under the conditions of a dilute solution and

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remains even in a certain range of a concentration corresponding to a semi-dilute regime providing only weak interpenetration (quasi-segregation) of branched macromolecules [4, 6, 11]. The concentration range corresponding to this so-called quasi-globular regime becomes larger and the intermolecular segregation becomes stronger as the degree of branching increases. Only at sufficiently large concentration due to the screening of intramolecular interactions the structure of the solution of branched polymers becomes in general equivalent to the structure of the solution of linear polymer chains.

Hence, the existing scaling theories give a valuable insight to the equilibrium structure and static properties of the solutions of uncharged branched polymers. At the same time our knowledge about the conformations of branched polyelectrolytes (branched polymers consisting of charged monomer units) in solutions is still incomplete. The main difference between the solutions of neutral polymers and polyelectrolytes is based on the different character of both intra- and intermolecular interactions determining the equilibrium conformational structure of macromolecules in the solution: these are short-range excluded volume interactions in the former case and long-range Coulomb forces in the latter case. This difference becomes, however, less pronounced in a salt-added solution due to the screening of Coulomb interactions.

Our analysis of star-branched polyelectrolyte conformations will be based on the scaling theories of linear weakly-charged polyelectrolytes in dilute [12–16], and semi-dilute [12, 17] solutions. The validity of a scaling approach for weakly charged polyelectrolytes, i.e. for flexible polymers with a small fraction of charged monomer units has been discussed in [15, 16].

At the same time some important results obtained for polyelectrolyte brushes, i.e. for the layers of polyelectrolyte molecules grafted at one end onto surfaces of different morphology and immersed into the solution [18–20], for strongly branched polyelectrolyte networks [21] and for block-copolymer micelles with charged coronas [22, 23] can be transferred to the description of static conformation of a star-branched polyelectrolyte.

After the description of the model, we shall consider the conformation of a single polyelectrolyte star in a dilute salt-free solution; the dependence of the star size on the number of branches will be of the main interest for us. The intramolecular conformational transition related to the collapse of the polyelectrolyte star due to a decrease in the solvent strength with respect to uncharged monomers interaction will be analyzed. Afterwards we present a scaling theory of semi-dilute salt-free solution of polyelectrolyte stars. Finally we discuss briefly the colloid crystalline ordering in the dilute solution of polyelectrolyte stars and the effect of screening of the Coulomb interaction in the salt-added solution on the polyelectrolyte stars conformation.

2. Model

Let us consider a star-branched macromolecule consisting of f linear branches (arms). Let N be the degree of polymerization of an arm (Fig. 1) and every m -th monomer carries an elementary charge e so that the total charge of the star-polyion is equal to $Q = fNe/m$. We assume the fraction m^{-1} of charged monomer units in the star to be small; the Bjerrum length $l_B = e^2/T\epsilon$, which characterizes the strength of the Coulomb interaction is of order of a monomer unit length a , so that the dimensionless coupling parameter $u = l_B/a \cong 1$. Here ϵ is the dielectric constant of the solvent and T is the temperature in the units of energy. The non-electrostatic interaction between uncharged monomers is described by the second, va^3 , and the third, $wa^6 \cong 1$, virial coefficients where the former one is dependent on the solvent strength, $v \cong \tau$ and $\tau = (T - \theta)/T$ is the relative deviation from the θ -point for uncharged polymer.

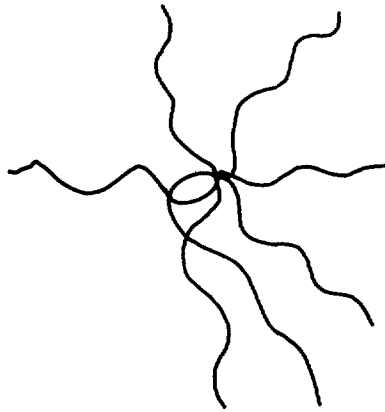


Fig. 1. — Star-branched polyelectrolyte: f is the number of branches, N is the length of every branch, N/m is the number of charges per branch.

Our analysis will be based on a scaling approach, which makes possible to obtain the power law dependences of the polyelectrolyte star size on the number of branches, on the degree of ionization, etc. We shall neglect all weaker (non-power) dependences and omit all the numerical coefficients. As will be shown below, this approximation is meaningful for polyelectrolyte stars formed by a large number of sufficiently long branches containing a small fraction of charged monomers.

3. Dilute Salt-Free Solution

We are starting our consideration with an analysis of the conformation of an individual polyelectrolyte star in a dilute salt-free solution where the average distance between stars exceeds by far their size. As we shall see below the screening of intra-star Coulomb repulsion in a dilute solution is weak if the number of arms is small, but becomes strong for many-arm stars. We focus our attention on the dependence of the star size on the number of branches f .

As is well known for neutral polymer stars [1–3], the repulsive short-range interaction between monomer units of different arms leads to an increase in the star size, $R(f)$, with respect to the size of a linear chain in the solution, $R(f = 1)$, in $f^{1/4}$ or $f^{1/5}$ times under the conditions of θ - or good solvent, respectively:

$$R(f) \cong \begin{cases} N^{1/2} a f^{1/4} & \theta \\ N^{3/5} a v^{1/5} f^{1/5} & + \end{cases} \quad (1)$$

(here and below we use notations “ θ ” and “+” for the conditions of θ - and good solvent, respectively).

If the total charge of a polyelectrolyte star is sufficiently large, then the main contribution to repulsive intra- and inter-arm interactions makes the Coulomb repulsion of charged monomers.

It is known that an isolated linear ($f = 1$) polyelectrolyte chain in a dilute salt-free solution loses counterions which appear to be spread almost uniformly over the volume of a solution. As a result charged monomers of the chains interact via unscreened Coulomb repulsive potential [12, 13].

The equilibrium conformation of the polyion is then determined by the balance between the energy of the Coulomb repulsion

$$F_{\text{Coulomb}}(R)/T \cong Q^2/\epsilon TR \quad (2)$$

and the elastic (conformational) free energy of the stretched chain [24,25] given by

$$F_{\text{elastic}}(R)/T \cong \begin{cases} (R/R_\theta)^2 & \theta \\ (R/R_+)^{5/2} & + \end{cases} \quad (3)$$

where $R_\theta \cong N^{1/2}a$ and $R_+ \cong N^{3/5}v^{1/5}a$ are the dimensions of a linear neutral chain under θ - and good solvent conditions, respectively. Minimization of the free energy gives

$$R_0(f=1) \cong \begin{cases} Nam^{-2/3}u^{1/3} & \theta \\ Nam^{-4/7}u^{2/7}v^{1/7} & + \end{cases} \quad (4)$$

(subscript "0" denotes the equilibrium value)

The polyelectrolyte chain partially stretched by intramolecular Coulomb repulsion according to equation (4) can be presented as a completely stretched chain of "electrostatic" blobs of size ξ_0 [12,13]. The chain sequence inside the blob remains unperturbed by electrostatic interactions and retains a Gaussian or an excluded volume statistics so that the blob size ξ_0 and the number of monomers per blob g_0 can be determined from equations

$$\frac{l_B(g_0/m)^2}{\xi_0} \cong 1, \quad (5)$$

$$\xi_0 \cong \begin{cases} g_0^{1/2}a & \theta \\ g_0^{3/5}av^{1/5} & + \end{cases} \quad (6)$$

which lead to

$$\xi_0 \cong \begin{cases} m^{2/3}u^{-1/3}a & \theta \\ m^{6/7}u^{-3/7}v^{2/7}a & + \end{cases} \quad (7)$$

It is easy to see that the blobs are Gaussian (θ -solvent conditions) at $v \ll m^{-2/3}u^{1/3}$, i.e. at $v\xi_0/a \ll 1$ and swollen (good solvent conditions) at $v \gg m^{-2/3}u^{1/3}$

The intramolecular Coulomb repulsion is strong enough to stretch the chain according to equation (4) if $\xi_0 \ll R_{\theta,+}$ that is the case at $m \ll N^{3/4}u^{1/2}$ or $m \ll N^{7/10}v^{-1/10}u^{1/2}$ under θ - or good solvent conditions, respectively. At larger m (i.e. if the fraction of charged monomers is smaller) the polyelectrolyte behaves like a neutral chain.

If the number of branches in the polyelectrolyte star is small, i.e. $f \geq 1$, the interaction between charged monomers of the star has also the character of unscreened Coulomb repulsion and can be described by equation (2) where now $Q = fNe/m$ is the total charge of the star. The elastic contribution to the free energy must take into account the stretching of all the branches: $F_{\text{elastic}}(R, f) = fF_{\text{elastic}}(R, f=1)$. Minimization of the free energy results in the equilibrium dimensions of star-branched polyelectrolyte:

$$R_0(f) \cong \begin{cases} Nam^{-2/3}u^{1/3}f^{1/3} & \theta \\ Nam^{-4/7}u^{2/7}v^{1/7}f^{2/7} & + \end{cases} \quad (8)$$

As follows from equation (8), the size of the star-branched polyelectrolyte retains the same dependence on the branch length N and on the degree of ionization m^{-1} as the size of a linear polyelectrolyte. However, the star size increases as a power function of the number of branches

f : $R_0(f)/R_0(f=1) \cong f^x$. The corresponding index is equal to $x_\theta = 1/3$ or $x_+ = 2/7$ under the conditions of θ - or good solvent, respectively (index $x = 1/3$ was obtained also in [22, 23] for spherical micelles formed by diblock copolymers with charged soluble block). Note that the same type of dependence of star size on the number of branches was found in [1-3] for neutral stars, but with smaller values of x : $x_\theta = 1/4$, $x_+ = 1/5$. We see that in both cases of θ - and good solvent the overall dimension of a polyelectrolyte star grows with f faster than the dimensions of a neutral polymer star under the corresponding solvent strength conditions.

The stretched branches of the polyelectrolyte star can be presented also as the sequences of electrostatic blobs of size $\xi_0(f) \leq \xi_0$ decreasing with an increase in f according to

$$\xi_0(f) \cong \begin{cases} m^{2/3} a u^{-1/3} f^{-1/3} \cong \xi_0 f^{-1/3} & \theta \\ m^{6/7} a u^{-3/7} v^{2/7} f^{-3/7} \cong \xi_0 f^{-3/7} & + \end{cases} \quad (9)$$

The crossover between θ - and good solvent conditions determined by equation $v\xi_0(f)/a \cong 1$ appears to be shifted towards larger values of v as the number f of branches increases. As follows from equations (8), (9) the polyelectrolyte effect is manifested in star-branched polymers at lower degree of chain ionization m^{-1} than in isolated branches: at $m \ll N^{3/4} u^{1/2} f^{1/8}$ or at $m \ll N^{7/10} u^{1/2} v^{-1/10} f^{3/20}$ under the conditions of θ - or good solvent, respectively. This means that even if a separated branch or the star with small number of branches exhibit a quasineutral behavior an increase in the number of branches can lead to the transition into polyelectrolyte regime at $f \geq f^\#$ where

$$f^\# \cong \begin{cases} N^{-6} m^8 u^{-4} & \theta \\ N^{-14/3} m^{20/3} u^{-10/3} v^{2/3} & + \end{cases} \quad (10)$$

if $m \leq m^*$ where

$$m^* \cong \begin{cases} N^{4/5} u^{2/5} & \theta \\ N^{10/13} u^{5/13} v^{-1/13} & + \end{cases} \quad (11)$$

According to equation (8) the size of a polyelectrolyte star grows with an increase in f rather slowly so that the ratio $Q(f)/R_0(f)$ also increases. As a result the growing fraction of counterions appear to be retained by the force of Coulomb attraction to the oppositely charged polyion. This fraction of counterions is localized in the volume occupied by a star-branched polyion thus partially neutralizing its charge. This phenomenon has been described for a dilute solution of charged colloidal particles in [26]. We discuss it in a more appropriate for star-branched polyelectrolyte manner in Appendix. As follows from equation (A.3), the fraction of counterions retained by the Coulomb attraction inside the star is negligible if $Q(f)l_B/(eR(f)) \ll 1$ that is the case if $f \ll f^*$ where f^* is defined by

$$f^* \cong \begin{cases} m^{1/2} u^{-1} & \theta \\ m^{3/5} u^{-1} v^{1/5} & + \end{cases} \quad (12)$$

For the stars with sufficiently small number of branches the effective (uncompensated) charge of the star is equal to $Q^* \cong Q$ and charged monomers of branches interact via unscreened Coulomb potential. Thus equations (8, 9) are valid at $f \ll f^*$ only.

Note that $f^* \gg 1$ if the condition of validity of the theory of weakly charged polyelectrolytes (average distance between the neighboring charges is larger than the Bjerrum length) is fulfilled.

If the condition $f \ll f^*$ is violated, i.e. for a polyelectrolyte star with sufficiently large number of branches, most of counterions are retained inside the star so that the volume occupied by the star is almost electroneutral as a whole, $Q^* \ll Q$. As follows from equation (12), the value of f^* grows as the solvent strength, v , increases. This means that a decrease in the

solvent strength may cause pumping of counterions into the star and partial neutralization of the star charge.

It has been discussed in [18, 19] and more accurately shown in [20] that the corresponding so called osmotic regime occurs for sufficiently dense polyelectrolyte brushes. As the main fraction of counterions in this regime is retained inside the brush, the stretching electrostatic force applied to grafted polyions is equal to the osmotic pressure of the gas of counterions inside the brush.

Using the same argument for many-arm polyelectrolyte star, we can write the osmotic stretching force-generating contribution to the free energy as a negative translational entropy of counterions in the volume occupied by a star:

$$F_{\text{osm}} \cong (Q(f)/e) \ln \frac{Q(f)}{eR^3}$$

Minimization of the free energy with respect to R gives the dimension of the polyelectrolyte star in the osmotic regime:

$$R_0(f) \cong \begin{cases} Nam^{-1/2} & \theta \\ Nam^{-2/5}v^{1/5} & + \end{cases} \quad (13)$$

As follows from equation (13), the star dimension in the osmotic regime does not depend on the number of branches in complete analogy to the independence of the polyelectrolyte brush thickness on the grafting density [18, 19].

In the framework of the blob picture the branches of a polyelectrolyte star can be presented in the osmotic regime as completely stretched chains of blobs of size

$$\xi_0(f) \cong \begin{cases} m^{1/2}a & \theta \\ m^{3/5}av^{1/5} & + \end{cases} \quad (14)$$

also independent of the number of branches f at $f \gg f^*$; as follows from equation (14) each of these blobs contains one charged monomer.

It is worth noting that in the osmotic regime not only total electroneutrality, but also local electroneutrality of the star takes place: it is easy to check that at $f \gg f^*$, where f^* is determined by equation (12), the Debye screening length provided by the concentration of counterions inside the star $\kappa^{-1} \cong \{l_B N f / (m R_0^3(f))\}^{-1/2}$ is smaller than the overall star size determined by equation (13).

Hence, the dimension of a polyelectrolyte star in a salt-free solution grows at $f \ll f^*$ with an increase in the number of branches according to equation (8) and becomes independent of f at $f \gg f^*$ according to equation (13). Thus a plateau on the dependence $R(f)$ appears. However, further increase in the number of branches gives rise to the monomer concentration inside the star that makes non-electrostatic excluded volume interactions between uncharged monomers stronger. At $f \gg f^{**}$, where

$$f^{**} \cong (N/m)^2 \quad (15)$$

these interactions begin to predominate over electrostatic interactions and the star size begins to grow again but now according to equation (1).

The results obtained in this section can be presented in a more spectacular manner with the aid of the diagram of states of a polyelectrolytestar in co-ordinates m, f (Fig. 2). Different

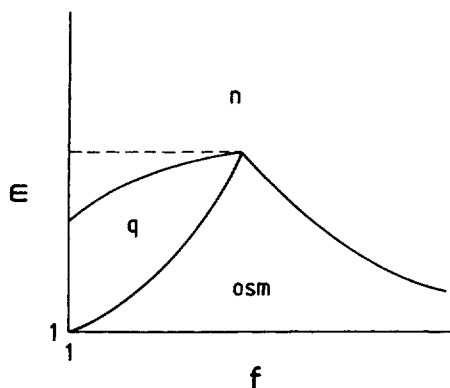


Fig. 2. — Diagram of states of a polyelectrolyte star in m, f co-ordinates (see the text for explanation).

regions of the diagram correspond to different regimes of the polyelectrolyte star behavior described above:

(**q**) a star with a small number of arms and unscreened Coulomb intra-star repulsion, $f^\# \ll f \ll f^*$, $Q^* \cong Q$;

(**osm**) an “osmotic” star retaining almost all counterions inside the star, $f^* \ll f \ll f^{**}$, $Q^* \ll Q$;

(**n**) a quasineutral star, in which non-electrostatic excluded volume interactions between uncharged monomers predominate over Coulomb interactions, $f \gg f^{**}$ or $f \ll f^\#$

The boundaries between regions **q/n**, **q/osm** and **osm/n** are described by equations (10), (12) and (15), respectively. As follows from the diagram, the non-electrostatic interactions in the star predominate over electrostatic ones at any f if $m \gg m^*$ where m^* is given by equation (11). At $m \ll m^*$ an increase in the number of branches f leads to the successive transition between **n-q-osm-n** regimes at $m^\# \ll m \ll m^*$ or, between **q-osm-n** regimes at $m \ll m^\#$, where $m^\#$ is given by

$$m^\# \cong \begin{cases} N^{3/4} u^{1/2} & \theta \\ N^{7/10} u^{1/2} v^{-1/10} & + \end{cases} \quad (16)$$

The schematic dependences of the size of a star-branched polyelectrolyte on the number of branches f are presented in Figure 3 for the cases of comparatively large, $m \ll m^\#$, and moderate, $m^\# \ll m \ll m^*$, fractions of charged monomer units. As follows from the curves, the difference between the sizes of neutral and polyelectrolyte stars as well as the range of f values, $f^\# \ll f \ll f^{**}$, where this difference is pronounced, become smaller as the fraction of charged monomers decreases.

4. Coil-Globule Transition in Polyelectrolyte Stars

In the preceding section we have considered the conformation of a polyelectrolyte star under the conditions of good or θ -solvent. In the former case both binary and ternary interactions between uncharged monomers have the character of short-range repulsion whereas in the latter case binary repulsion and attraction compensate each other. If electrostatic intramolecular interactions predominate over non-electrostatic interactions of uncharged monomers (polyelectrolyte regime) then the difference between the star conformation under good and θ -solvent conditions is not of principal character and is manifested mostly on the scale of the stretching

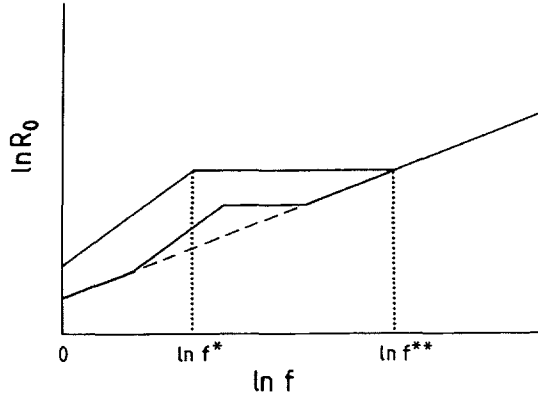


Fig. 3. — Schematic dependence of the size of a star-branched polyelectrolyte on the number of branches f in a dilute salt-free solution (solid lines) for $m \ll m^\#$, the upper curve, and for $m^\# \ll m \ll m^*$, the lower curve; the dashed line gives the same dependences for a neutral star polymer, $m \gg m^*$.

ξ_0 -blobs which are swollen in the former case and Gaussian in the latter case. However, if the solvent strength decreases far below the θ -point, ($v \sim \tau \leq 0$), i.e. binary excluded volume interactions between uncharged monomers acquire the character of a strong short-range attraction the collapse transition in the star occurs.

Let us review briefly the main ideas and results concerning the collapse transitions in uncharged polymer stars [5] on the one hand and in linear polyelectrolytes [14] on the other hand.

A decrease in the solvent strength, τ , (usually associated with a decrease in temperature, T) causes continuous decrease in the dimension of a **neutral star polymer**. At sufficiently low temperature below the θ -point ($\tau \leq 0$) the star passes into collapsed (globular) state. In this state the intramolecular monomer density and, consequently, the overall star dimension are determined by the balance between attractive binary and repulsive ternary inter-monomer interactions, $fN/R^3(f) \cong |v|$, and the star forms a globule of a spherical shape corresponding to the minimum of the surface free energy, $F_s \cong \gamma R^2(f)$, where the surface tension coefficient is given by

$$\gamma \cong T|v|^2 a^{-2} \cong T\xi_t^{-2}$$

and we have introduced the “thermal” correlation length $\xi_t \cong a|v|^{-1}$ equal to the size of the part of the chain in the globule which remains unperturbed by excluded volume interactions and retains Gaussian statistics. Due to strong repulsion of star arms under θ -solvent conditions, the θ -range (or the transition range), $\Delta v \cong N^{-1/2} f^{1/4}$, becomes wider as f increases and the transition into the collapsed state occurs at larger $|v|$ than the corresponding transition in a linear chain consisting of N monomers. Note that the width of the transition range Δv tends to zero as N tends to infinity so that the coil-globule transition in a star macromolecule has the character of a second order phase transition (see [5] for further details).

The binary attractive interactions between uncharged monomer units of **weakly charged polyelectrolyte chain** are able to compete, at least at sufficiently large $|v|$, with an electrostatic repulsion between charged monomers and lead to the polyelectrolyte globule formation. The local structure of the polyelectrolyte globule formed by one weakly charged linear chain coincides with that of a neutral polymer globule and is characterized by the same local

monomer density proportional to $|v|$ and the correlation length $\xi_t \cong a|v|^{-1}$. At the same time the total dimension of the collapsed polyion is determined by the balance between the Coulomb repulsion of charged monomers and the surface tension at the globular interface. As a result the polyelectrolyte globule remains partially stretched, $R \sim N$, by the intramolecular Coulomb repulsion and can be presented as a sequence of collapsed blobs each of size D equal to the globule thickness. The equilibration of two R -dependent contributions into the free energy, i.e. of the Coulomb repulsion given by equation (2) and of the surface free energy given by

$$F_s/T \cong \gamma RD/T \quad (17)$$

where the globule thickness is $D \cong (R|v|a/N)^{-1/2}$, results in

$$R_g \cong Nam^{-4/3}u^{2/3}|v|^{-1} \cong Na^2\xi_0^{-2}\xi_t \quad (18)$$

$$D_g \cong m^{2/3}u^{-1/3}a \cong \xi_0. \quad (19)$$

(here and below in this section we shall use the notation $\xi_0, \xi_0(f)$ for the size of an electrostatic blob defined by equation (7 θ), (9 θ) under θ -solvent conditions). The range of validity of equations (18), (19) corresponding to the collapsed state of a polyelectrolyte chain (collapsed ξ_0 -blobs) is determined by the condition $R_g \ll R_0^{(\theta)}$ that is the case at $\xi_t \ll \xi_0$ or $|v| \gg |v^*|$ where $|v^*| \cong m^{-2/3}u^{1/3}$. At smaller $|v|$ the ξ_0 -blobs remain Gaussian and the polyion size is given by equation (4 θ). As the collapse transition occurs on the scale of every ξ_0 -blob independently, the coil-globule transition in a polyelectrolyte chain has the character of a smooth non-phase conformational transition.

However, further decrease in the solvent strength (an increase in $|v|$) leading, according to equation (18) to a decrease in the polyelectrolyte globule length, R_g , results in an increase in the linear charge density Q/R_g . At $Ql_B/(eR_g) \cong 1$ or at $|v| \cong |v^{**}|$ where

$$|v^{**}| \cong m^{-1/3}u^{-1/3} \quad (20)$$

the Manning-type condensation of counterions on the charged cylindrical globule starts; a fraction $(Q - Q^*)/Q$ of counterions becomes localized in the space inside the globule partially neutralizing the polyion charge and providing the effective linear charge density equal to $Q^*/R_g \cong e/l_B$. A decrease in the effective globule charge leads to a decrease in the globule length, R_g . The main point here is that according to equation (18) the globule length, R_g , decreases with a decrease in an effective globule charge Q^* faster than Q^* so that the linear charge density $Q^*/R(Q^*)$ increases with a decrease in Q^* . As a result an avalanche-like counterion condensation accompanying by an abrupt collapse leading to the formation of ordinary spherical globule of size $R_g \cong (Na^3/|v^{**}|)^{1/3}$ occurs. This globule accumulate almost all its counterions, $Q^* \ll Q$. However, it is easy to prove, that at $|v| \geq |v^{**}|$ the counterions osmotic pressure do not affect significantly the globule conformation. Further increase in $|v|$ leads to a continuous decrease in the globule size, $R_g \sim |v|^{-1/3}$

Let us mention that classical Manning condensation of counterions occurs only on an infinite cylindrical polyion. However, this result can be applied to charged cylindrical globules of finite length if the electrostatic field created by a charged globule has a cylindrical symmetry on the scale larger or at least comparable to the Debye screening length that is usually the case in the solutions of small but finite concentration of polyelectrolyte or salt.

Note, that an abrupt collapse with the avalanche-like condensation of counterions occurs if the linear charge density on the chain is sufficiently large, $m \ll N^{3/5}u^{4/5}$. In the intermediate range of chain ionization, $N^{3/5}u^{4/5} \ll m \ll N^{3/4}u^{1/2}$ a decrease in the solvent strength results in smooth crossover between polyelectrolyte and quasineutral globule at $|v| \cong Nm^{-2}u$.

The coil-globule transition in **polyelectrolyte stars** with small number of branches, $f \ll f^* \cong m^{1/2}u^{-1}$, retains many features of the similar transition in a single polyelectrolyte chain. The basis of this similarity is, of course, the same character of intramolecular electrostatic interaction, i.e. unscreened Coulomb repulsion.

The coil-globule transition in the polyelectrolyte star starts with the collapse of individual electrostatic stretching blobs at $|v| \cong |v^*(f)|$ where

$$|v^*(f)| \cong a/\xi_0(f) \equiv f^{1/3}m^{-2/3}u^{1/3}, \quad f \ll f^* \quad (21)$$

(or at $\xi_t \cong \xi_0(f)$); note that at $f \gg 1$ we have $|v^*(f)| \gg |v^*(f=1)|$. The shift of the transition point towards lower temperatures becomes larger as f increases. At $v \cong v^*(f)$ the star size is given by equation (8) and all the contributions to the free energy of the star, F_{Coulomb} , F_{elastic} , F_s and the free energy of volume interactions $F_{\text{vi}} \cong -Na^2\xi_t^{-2}$ are of the same order of magnitude $\cong Nfa^2/\xi_0^2(f)$.

At $|v| \geq |v^*(f)|$ a decrease in the solvent strength, i.e. in v , leads to a decrease in the extension of star branches. Thus the energy of intra- and inter-branch Coulomb repulsion increases. Simultaneously the surface tension at the interface between collapsing branches and the solution increases too leading to an effective attraction of branches. Consequently one can imagine two scenarios of a star collapse: (i) every branch collapses separately, the star retains a spherical symmetry; (ii) the effective attraction of collapsed branches overcomes their Coulomb repulsion causing the sticking of branches in a cylindrical globule.

Let us start with the first scenario which occurs at sufficiently small f . At $|v| \geq |v^*(f)|$ the radial dimension R of branches is determined by the balance between $F_{\text{Coulomb}}(f) \cong Q(f)^2/(\epsilon R)$ and the total surface free energy $F_s(f) \cong fT\xi_t^{-2}RD$, where the thickness of every branch D is determined by the condition $D \cong a(N\xi_t/R)^{1/2}$. As a result we get

$$R_g(f) \cong Nam^{-4/3}u^{2/3}|v|^{-1}f^{2/3} \cong Na^2\xi_0^{-2}(f)\xi_t \quad (22)$$

$$D_g(f) \cong \xi_0(f) \quad (23)$$

$$F_{\text{Coulomb}}(f)/T \cong F_s(f)/T \cong Nf^{4/3}u^{1/3}m^{-2/3}|v| \cong Na^2f\xi_0^{-1}(f)\xi_t^{-1} \quad (24)$$

As follows from equations (22, 23) a decrease in the solvent strength causes continuous decrease in the radial dimension of collapsed branches $R_g(f)$ whereas their thickness $D_g(f)$ remains constant and equal to the size of electrostatic blob $\xi_0(f)$ under θ -solvent conditions. Comparison with equations (18, 19) shows that the branches of collapsing star are stretched in $f^{2/3}$ times with respect to the size of collapsing linear polyelectrolyte chain whereas their thickness is $f^{1/3}$ times smaller.

If $m \gg N^{3/5}u^{4/5}f^{1/2}$ a decrease in the solvent strength results finally in the continuous crossover with a state of quasineutral spherical globule. This crossover occurs at $|v| \cong Nm^{-2}f^{1/2}u$; note that this point corresponds to the condition of close packing of $\xi_0(f)$ blobs at the globule interface: $R_g^2(f) \cong f\xi_0^2(f)$.

At larger fraction of charged monomers, when $m \ll N^{3/5}u^{4/5}f^{1/2}$ the continuous collapse of a star polyelectrolyte described by equations (22, 23, 24) is interrupted by an avalanche-like accumulation of counterions into the globule and an abrupt collapse of a star polyelectrolyte globule occurs at $|v| \cong |v^{**}(f)| \cong m^{-1/3}u^{-1/3}f^{-1/3}$

The reasons of the avalanche-like character of accumulation of counterions inside the star-globule accompanying its abrupt collapse are, of course, a strong dependence of the globule size on its effective charge, $R_g(f) \sim Q^{*4/3}$, (see Eq. (22)) and the relation between the effective charge Q^* and the size of a star given by equation (A.3).

Let us note that $|v^{**}(f)| \gg |v^*(f)|$ if $f \ll f^*$.

As has been discussed above at $|v| \geq |v^*(f)|$ the free energy losses at the interfaces of collapsing branches causes their effective attraction which can overcome the inter-arm Coulomb repulsion.

Let us consider the second scenario when at $|v| \cong$ or $\geq |v^*(f)|$ the star loses the spherical symmetry and all the branches stick together forming a cylindrical globule.

At $|v| > |v^*(f)|$ the length of a cylindrical globule, R , is determined by the balance between Coulomb repulsion, F_{Coulomb} , which is still given with the accuracy of a logarithmic factor by equation (2), and the overall elasticity of all the branches, $F_{\text{elastic}} \cong fR^2/(Na^2)$, and remains (in our approximation) equal to the star size in the θ -point, $R_g(f) \cong Na^2\xi_0^{-1}(f)$. An increase in $|v|$ over $|v^*(f)|$ results in a decrease in the globule thickness according to

$$D_g(f) \cong f^{1/3}(\xi_t \xi_0)^{1/2} \quad (25)$$

while $F_{\text{Coulomb}}(f)/T \cong F_{\text{elastic}}(f)/T \cong Nfm^{-4/3}u^{2/3}\ln R_0(f)$ remain virtually constant and larger than the surface free energy F_s/T until $D_g \gg \xi_0$ that takes place at $\xi_t \gg f^{-1/3}\xi_0(f)$ i.e. at $|v| \ll |v^\#(f)|$ where

$$|v^\#(f)| \cong f^{1/3}|v^*(f)| \quad (26)$$

Taking into account equation (24) we get that the sticking of branches occurs at $|v| \cong |v^*(f)|\ln R_0$

Thus the range of $|v|$ where the globule thickness decreases according to equation (25) at constant globule length really exist, i.e. $|v^\#(f)| \gg |v^*(f)|\ln R_0$, only if $f^{1/3} \gg \ln R_0(f)$.

At larger $|v| \geq |v^\#(f)|$ the length of the globule is determined by the balance between the surface free energy and Coulomb repulsion and decreases with a decrease in the solvent strength (decrease in ξ_t) according to

$$R_g(f) \cong fNa^2\xi_t\xi_0^{-2} \quad (27)$$

whereas the globule thickness $D_g(f) \cong \xi_0$ is independent of $|v|$ and of f . Thus the dimensions of the globule formed by f -arm polyelectrolyte star coincide with those of the globule formed by linear polyelectrolyte chain consisting of fN monomers. In other words, the topology of the polyelectrolyte molecule affects the position of the beginning of the collapse transition and does not affect the globule shape and dimensions in the depth of the globular regime.

The free energy of the cylindrical globule at $|v| \gg |v^\#|$ is given by

$$F_{\text{Coulomb}}(f)/T \cong F_{\text{elastic}}(f)/T \cong Nfm^{-2/3}u^{1/3}|v|\ln R_0(f) \quad (28)$$

Comparison of equations (24) and (28) shows that at $|v| \geq m^{-2/3}u^{1/3}f^{1/3}\ln R_0$ the cylindrical globule with sticked branches is energetically more favorable than the star-globule consisting of separately collapsing branches if $(\ln R_0)^3 \ll f \ll f^*$ i.e. in a sufficiently narrow range of f .

A decrease in the length of the cylindrical globule at $|v| \gg |v^\#(f)|$ according to equation (27) leads to an increase in the linear charge density $Q(f)/R_g(f)$ which coincides with the linear charge density on the cylindrical globule formed by linear polyelectrolyte chain at the same $|v|$. Correspondingly, the avalanche-like process of counterions condensation and an abrupt collapse of the star-polyelectrolyte globule starts at $|v| \cong |v^{**}| = \text{const}(f)$ given by equation (20). At $|v| \geq |v^{**}|$ the polyelectrolyte star forms an ordinary spherical globule of size $R_g(f) \cong (fNa^3/|v|)^{1/3}$. As we have already mentioned, this globule contain almost all counterions, but at $|v| \geq |v^{**}| \gg m^{-1/2}$ the negative osmotic pressure related to monomer-monomer attraction, $\pi_{vi} \cong -|v|^3$, is stronger than the osmotic pressure of counterions, $\pi_{ci} \cong |v|/m$, so that the dimension of the globule formed by the polyelectrolyte star is the same as the dimension of a

neutral globular star polymer. Note that as the number of arms f in the star grows, the range of stability of the cylindrical globule described by equation (27) decreases:

$$\left| \frac{v^{**}}{v^{\#}(f)} \right| \cong \left(\frac{f^*}{f} \right)^{2/3}$$

A continuous transition between cylindrical globule formed by sticked branches and ordinary spherical globule where non-electrostatic interactions predominate over electrostatic ones is possible if the fraction of charged monomers is small enough, $m \gg N^{3/5} u^{4/5} f^{3/5}$ and occurs at $|v| \cong N f m^{-2} u$.

Finally let us discuss the collapse transition in many-arm polyelectrolyte stars, $f \gg f^* \cong m^{1/2} u^{-1}$. In this case the collapse of star branches start at $\xi_t \cong \xi_0(f)$ given by equation (14) or at $|v| \cong v^*(f)$ where

$$|v^*(f)| \cong m^{-1/2}, \quad f \gg f^*. \quad (29)$$

As the star accumulates almost all the counterions under the θ -solvent condition, the collapse occurs under the conditions of osmotic regime. At the same time, at $|v| \geq m^{-1/2}$ the attraction of uncharged monomers in the globule is stronger than the osmotic pressure of counterions, $|\pi_{vi}| \geq \pi_{ci}$, so that the polyelectrolyte star form an ordinary spherical globule. The difference in the monomer density in the collapsed (globular) and stretched (θ) states indicates the abrupt character of the coil-globule transition which occurs in a polyelectrolyte star with a large number $f \gg f^*$ of branches at $|v| \cong m^{-1/2}$. Note, that at the same value of $|v|$ a collapse transition in osmotic polyelectrolyte brushes occurs regardless of their morphology (see [18, 19]).

5. Semi-Dilute Salt-Free Solution of Polyelectrolyte Stars

Our analysis of conformations of weakly-charged star-branched polyelectrolyte in semi-dilute solution is based on the assumption that only one characteristic length scale coinciding with the Debye screening length in the solution exists. This assumption has been proved for linear weakly charged polyelectrolytes in [15,16] and makes possible the consideration based on scaling arguments.

Let us describe first following the lines of [12, 17] the conformation of one linear weakly charged chain in a semi-dilute solution supposing that the electrostatic screening length scales with the solution concentration c as $\kappa^{-1}(c) \cong (l_B c/m)^{-1/2}$, i.e. according to the Debye law, at least at concentrations above the overlapping threshold. It seems to be natural to define c^* as a concentration at which the electrostatic screening length becomes equal to the dimension R_0 of an isolated polyion in a dilute solution given by equation (4), i.e. form the condition $\kappa(c^*)R_0 \cong 1$. As a result we obtain

$$c^* \cong \begin{cases} N^{-2} m^{7/3} u^{-5/3} a^{-3} & \theta \\ N^{-2} m^{15/7} u^{-11/7} v^{-2/7} a^{-3} & + \end{cases} \quad (30)$$

At $c \ll c^*$ we have $\kappa R_0 \ll 1$, i.e. intramolecular electrostatic interactions are not screened and polyions retain the same conformation as in a dilute solution. It is worth noting that at $m \gg 1$, i.e. for weakly charged polyelectrolytes the concentration c^* defined by equation (30) is larger than the overlapping concentration $c_{\text{overlap}} \cong N/R_0^3$; due to strong stretching of polyions in the dilute solution the overlapping concentration is not sufficiently large to provide the screening of electrostatic interactions on the scale of polyions dimension. (Let us also note that this situation is similar to the situation in a semi-dilute solution of neutral semi-flexible

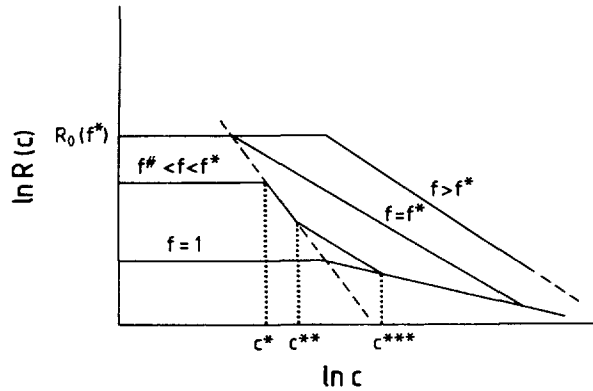


Fig. 4. — Schematic dependence of the dimension of a star-branched polyelectrolyte on the concentration of the solution.

polymers where due to the local chain stiffness the screening at the overlapping concentration is also too weak to affect the chain dimension [27, 28]).

At $c \gg c^*$ the solution is characterized by a correlation length ξ which must tend to R_0 at $c \cong c^*$, scale as some power of (c/c^*) and be independent of N at $c \gg c^*$. These requirements are satisfied by

$$\xi(c) \cong R_0(c/c^*)^{-1/2} \cong (l_B c/m)^{-1/2} \quad (31)$$

i.e. $\xi(c)$ coincides with the Debye screening length κ^{-1}

The size of the polyelectrolyte chain also must tend to R_0 at $c \cong c^*$, scale as some power of (c/c^*) and be proportional to $N^{1/2}$ at $c \gg c^*$; these arguments result in

$$R(c) \cong R_0(c/c^*)^{-1/4} \cong (R_0 \kappa^{-1})^{1/2} \cong \begin{cases} N^{1/2} (mu)^{-1/12} (c/a)^{-1/4} & \theta \\ N^{1/2} m^{-1/28} u^{-3/28} v^{1/14} (c/a)^{-1/4} & + \end{cases} \quad (32)$$

The polyion dimension given by equation (32) is the dimension of the Gaussian chain of "superblobs" of size $\xi(c)$; each of them contains $(\xi(c)/\xi_0)g_0$ monomers (where ξ_0 and g_0 are given by Eqs. (5),(7)) i.e. on the scale smaller than $\xi(c)$ the chain retains the same structure as in a salt-free solution whereas on a larger scale it becomes a random coil.

At large concentration the polyelectrolyte effects are suppressed due to strong screening and the polyelectrolyte chain size tend to that of a neutral chain in a semi-dilute solution. Under the θ -solvent conditions the chain size given by equation (32) tend to $N^{1/2}a$ at $c \cong (mu)^{-1/3}a^{-3}$; note that simultaneously the screening length, $\xi(c)$, becomes equal to the electrostatic blob size, ξ_0 . In the case of a good solvent the range of validity of the equation (32) and approximation used in general is expected to be limited by the condition $\kappa^{-1} \gg \xi_c$, where $\xi_c \sim v^{1/4}c^{-3/4}$ is the correlation length in a semi-dilute solution of neutral chains.

Of course, equations (31, 32) present an extension of the scaling picture of the semi-dilute linear polyelectrolyte solution [12, 17] for the case of weakly charged ($m \gg 1$) chains and arbitrary solvent strength.

Let us consider now the semi-dilute regime for the solution of polyelectrolyte stars with a small number of branches, $f \ll f^*$. We define the concentration $c^*(f)$ corresponding

to the crossover between dilute and semi-dilute solutions from the condition $\kappa^{-1}(c^*(f)) \equiv (m/(uc^*(f)))^{1/2} \cong R_0(f)$. Thus $c^*(f)$ is given by

$$c^*(f) \cong c^*(f=1) \cdot \begin{cases} f^{-2/3} & \theta \\ f^{-4/7} & + \end{cases} \quad (33)$$

Note, that $c^*(f)$ defined by equation (33) decreases with an increase in f remaining at $f \ll f^*$ greater than the stars overlapping concentration. At $c \gg c^*(f)$ the correlation radius of the solution scales like

$$\xi(c) \cong R_0(f)(c/c^*(f))^{-1/2} \cong \kappa^{-1}(c) \quad (34)$$

The concentrational dependence of the star size can be obtained with the aid of the following arguments: (i) at $c \gg c^*(f)$ the star size must scale like

$$R(f, c) \cong R_0(f)(c/c^*(f))^\alpha$$

(ii) at large c the structure of the solution must coincide with that of a semi-dilute solution of linear polyelectrolyte chains (individual branches), $R(f, c) \cong R(f=1, c)$; (iii) at $f \cong 1$ we must recover the dependence $R(c)$ for the linear chains in the whole range of c . The only function which obeys all these conditions is

$$R(f, c) \cong R_0(f) \left(\frac{c}{c^*(f)} \right)^{-1/2} \cong \kappa(c)^{-1} \quad (35)$$

in the range of $c^*(f) \ll c \ll c^*(1)$ and $R(f, c) \cong R(f=1, c)$, where $R(f=1, c)$ is given by equation (32), at $c \gg c^*(f=1)$. Equation (35) describes a contraction of a polyelectrolyte star in the whole range of $c^*(f) \ll c \ll c^*(f=1)$ only for stars with a small number of branches $f \ll \tilde{f} \ll f^*$ where \tilde{f} is given by

$$\tilde{f} \cong \begin{cases} m^{1/3}u^{-2/3} & \theta \\ m^{3/7}u^{-5/7}v^{1/7} & + \end{cases} \quad (36)$$

It is easy to see, that according to equation (35) the star size decreases due to the screening of the intramolecular Coulomb repulsion by counterions with an increase in c faster than $c^{-1/3}$, i.e. the degree of star overlapping diminishes. Hence, for stars with a larger number of arms, $\tilde{f} \ll f \ll f^*$, the concentration $c^{**}(f)$ exists, $c^*(f) \ll c^{**}(f) \ll c^*(f=1)$, at which $R(f, c^{**}(f)) \cong (fN/c^{**}(f))^{1/3}$ and simultaneously $R(f, c^{**}(f)) \cong uaQ/e$. It is easy to find that

$$c^{**}(f) \cong c^*(f) \cdot \begin{cases} (f^*/f)^{4/3} & \theta \\ (f^*/f)^{10/7} & + \end{cases} \quad (37)$$

Thus at $c \geq c^{**}(f)$ the star size can decrease with an increase in c not faster than $R(f, c) \cong (fN/c)^{1/3}$ tending at $c \cong c^{***}(f)$ where

$$c^{***}(f) \cong c^{**}(f) \left(\frac{f}{\tilde{f}} \right)^6 \quad (38)$$

to the individual branch size in the solution of equivalent linear chains of the same concentration (Eq. (32)). At higher concentration the structure of the solution coincides in general with that of the solution of individual branches.

Let us turn now to stars with a large number of arms, $f \gg f^*$, but $f \ll f^{**}$. In this case the intra-star Coulomb interactions are partially screened already in an individual star under

the conditions of a dilute solution. Hence, the crossover concentration $c^*(f)$ is equal to the overlapping concentration:

$$c^*(f) \cong fN/R_0^3(f) \cong \begin{cases} N^{-2}m^{3/2}fa^{-3} & \theta \\ N^{-2}m^{6/5}v^{-3/5}fa^{-3} & + \end{cases} \quad (39)$$

Note that at $f \cong f^*$ both definitions of $c^*(f)$, equations (33), (39), coincide with each other. According to equation (39) the crossover concentration $c^*(f)$ grows with an increase in f at $f \gg f^*$. The correlation radius of the solution at $c \gg c^*(f)$ is still described by equation (34) i.e. is equal to the Debye screening length. The scaling function describing a decrease in the size of a star at $c \gg c^*(f)$ should meet the conditions (i), (ii) discussed above for the case $f \ll f^*$ and provide a smooth crossover with a concentrational dependence of the star size at $f \cong f^*$. These conditions can be satisfied if

$$R(c, f) \cong (fN/c)^{1/3} \quad (40)$$

The decrease in the star size proportionally to $c^{-1/3}$ according to equation (40) occurs in the range of $c^*(f) \ll c \ll c^{***}(f)$ where the concentration $c^{***}(f)$ is given by

$$c^{***}(f) \cong c^*(f)f^3 \begin{cases} f^{*-1} & \theta \\ f^{*-9/7} & + \end{cases} \quad (41)$$

At $c \cong c^{***}$ the star size reaches the size of an individual arm in a semi-dilute solution and further decrease in the star size with an increase in c occurs according to equation (32).

If the number of branches exceeds $(N/m)^2$, i.e. non-electrostatic interactions in an isolated star predominate over Coulomb interactions, the crossover concentration c^* is given by $c^*(f) \cong fN/R^3(f)$ where the star size $R(f)$ is now given by equation (1). In the concentration range $c^*(f) \ll c \ll c^{***}(f)$ where

$$c^{***}(f)/c^*(f) \cong \begin{cases} f^{3/4} & \theta \\ f^{6/5} & + \end{cases}$$

the star size decreases with an increase in c as $R(f, c) \cong (fN/c)^{1/3}$ [4]. At the second crossover concentration c^{***} the branches of stars loses their stretching with respect to the linear chains dimension in a semi-dilute solution of the same concentration. At $c \gg c^{***}$ the structure of the solution is equivalent, in general, to the structure of the solution of individual branches.

6. Concluding Remarks and Discussion

The analysis of conformations of star-branched polyelectrolytes in dilute and semi-dilute salt-free solutions shows that a significant difference in the behaviour of stars with small and large numbers of branches exists. In contrast to neutral stars, the characteristic number of branches f^* distinguishing many- and few-arm stars is not of order of unity but increases proportionally to some power of inverse fraction of charged monomers, $m \gg 1$. Of course, this difference disappear for strongly charged, $m \cong 1$ branched polyelectrolyte.

The main difference between few- and many-arm stars is related to the different character of counterion distribution and, consequently, to the different character of intramolecular Coulomb interaction in a dilute solution. The stars with a small number of arms, $f \ll f^*$, are unable to retain the counterions which spread almost uniformly all over the solution volume; the intramolecular electrostatic interaction in this case has a character of unscreened Coulomb repulsion. As a result, the star size grows with an increase in f according to some power law. In contrast to the former case, the stars with a large number of branches $f \gg f^*$

have sufficiently large charge to retain almost all counterions in the intra-star space; thus the Coulomb interaction between charged arms becomes partially screened and the star size does not further grow with an increase in f . Only at very large number of arms, $f \gg f^{**}$, the star passes into quasineutral regime where an increase in the star size with f results from non-electrostatic excluded volume interactions between uncharged monomers of the branches. Note that the value of f^* increases with an increase in the solvent strength whereas the value of f^{**} does not depend on it.

The difference between many- and few arm stars is well manifested in the character of the conformational transition related to the collapse of a star caused by a decrease in a solvent strength below the θ -point. If $f \ll f^*$, the collapse of the star begins with a sticking of the branches together and with a loss of the spherical symmetry of the star; all this occur at a certain value of $|v| \cong |v^*(f)|$ which increases with an increase in f . The stars with a large number of branches, $f \gg f^*$, collapse far below the θ -point at $|v| \cong m^{-1/2}$ independently of the number of branches retaining the spherical symmetry.

As has been shown in [12], the Coulomb repulsion between linear polyelectrolyte molecules in a dilute salt-free solution can result in the formation of periodic 3-dimensional lattice in analogy to a colloid crystalline order. The corresponding concentration range is determined by the condition $Q^2/(\epsilon T r) \geq 1$, where r is the distance between neighboring polyions in the solution on the one hand, and by the condition of weak screening $\kappa(c)r \ll 1$ on the other hand. Simple consideration results in the lower concentration limit for colloid ordering $\tilde{c} \sim N^{-5}m^6$ whereas the upper limit \tilde{c} corresponding to the melting of the colloid crystal due to the screening of intermolecule Coulomb repulsion by counterions can be associated with c^* . The picture of colloid ordering in a dilute solution of polyelectrolyte stars also depends on the number of branches in the stars. If $f \ll f^*$ i.e. counterions are spread uniformly in the solution, then the boundaries of the lattice regime, \tilde{c} and \tilde{c} are the same as for linear polyelectrolyte of the same total molecular weight, because they are determined by the total polyion charge Q only. However, if $f \gg f^*$ then the effective charge of the polyions and a number of free counterions delegated by every polyion to the solution are dependent on the polyions size (the problem has been studied for charged spheres of fixed size in [26]). As a result, the lattice regime occurs in the range of interstar separation $R_0 \ll r \ll R_0^2/l_B$. As R_0 is independent of f at $f \gg f^*$ and $c \cong fN/r^3$, for stars with a large number of branches the lattice regime occurs at comparatively large concentrations of the solution.

Our scaling analysis based on the assumption of the Debye screening in a semi-dilute solution of polyelectrolyte stars indicates the manifestation of a quasiglobular behaviour, $R \sim c^{-1/3}$, in the intermediate range of the solution concentration. Thus an analogy between the behaviour of neutral and charged branched polymers in a semi-dilute solution can be established.

All the predictions concerning an influence of the number of branches, f , and of the fraction of charged monomers, $1/m$, on the conformations of star-branched polyelectrolytes are expected to be qualitatively valid in a wide range of parameters f, m and N . At the same time, the power-law dependences of the star size (gyration radius) on these parameters which can be measured in an experiment have an asymptotic character, i.e. one can observe them only for the stars with sufficiently large number $f \gg 1$ of long weakly charged branches in a corresponding concentration range.

It is easy to see, that if the fraction of charged monomers is ~ 0.1 and the length of branches is $N \sim 10^2$, the characteristic numbers of branches are $f^* \geq 1$ and $f^{**} \sim 10^2$. At the moment the problem of synthesis of sufficiently monodisperse samples of neutral polymer stars with a large number of branches $f \geq 10^2$ is solved [7, 8] that has made possible to check the main predictions of scaling theories [1, 3, 4] concerning the effect of the number of branches on the equilibrium conformations of neutral stars in dilute and semi-dilute solutions.

The problem of charging of a small fraction of monomers in a star can be solved by substituting of homo-polymer branches by co-polymer containing a small fraction of strongly dissociated ionizable monomer groups. Another way is to synthesize a star of a weak polyelectrolyte characterized by a small degree of ionization in the solution. However, in the latter case an increase in the number of branches will affect the local ionization balance in the star that will result in a much more complicated behaviour (see relevant discussion for the case of a planar polyelectrolyte brush in [29]).

Finally, let us discuss briefly the conformation of polyelectrolyte stars in a salt-added solution starting from the case of a large number of branches, $f \gg f^*$, corresponding to "osmotic" stars. An equivalent system has been analyzed in details in [21]. The added salt begins to affect the star branches conformation when the salt concentration, ϕ_s , becomes large enough to provide the screening length κ_s^{-1} smaller than the screening length due to counterions in the osmotic star in a salt-free solution. In this salt-dominance regime the intra-star Coulomb interactions are partially screened mostly due to salt ions and can be described in terms of an effective second virial coefficient $v_{\text{eff}} \cong (a^3 m^2 \phi_s)^{-1}$. The star size is given then by equation (1+) with v substituted by v_{eff} . The collapse of the star due to a decrease in the solvent strength occurs abruptly at $|v| \cong m^{-1/2}$ if $\phi_s \ll m^{-3/2}$ (no salt dominance in the collapsed state) or gradually as in neutral stars at $|v| \cong v_{\text{eff}}$ if $\phi_s \gg m^{-3/2}$.

The screening effects in the star with a small number of branches, $f \ll f^*$, become significant when $\kappa_s^{-1} \leq R_0(f)$ where the star size $R_0(f)$ is given by equation (8). As the salt-dominance condition is simultaneously fulfilled, the electrostatic interactions in the star can be described as in the former case with the aid of an effective second virial coefficient v_{eff} .

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Appendix A

Counterions Distribution

In this Appendix we rederive following the lines of [22, 26] in the most convenient for our purposes manner the result concerning the counterion condensation onto a spherically distributed immobilized charge. So let the immobilized charge Q be uniformly spread in a spherical core of radius R which is localized in the center of a spherical shell of total volume $V + (4/3)\pi R^3$, $V \gg R^3$. We suppose all the space inside the shell (including the core) to be filled by the solvent (continuous dielectric medium with a constant ϵ); the shell as a whole is electroneutral, i.e. contains also Q/e mobile counterions which can freely move inside the shell and also penetrate into a core region where immobilized charge is localized. For simplicity we suppose the charge density related to mobile counterions to be constant (though different) inside and outside the core. Let $(Q/e - Q^*/e)$ counterions are localized in the core region so that the effective (uncompensated) charge of the core is equal to Q^* and the number of counterions in the outer solution is Q^*/e . The total free energy of the system can be presented as

$$F/T \cong \frac{Q^*}{e} \ln\left(\frac{Q^*}{eV}\right) + \frac{Q - Q^*}{e} \ln\left\{\frac{Q - Q^*}{eR^3}\right\} + \frac{Q^{*2}}{\epsilon TR} \quad (\text{A.1})$$

where the first and the second terms describe the translational entropy of counterions outside and inside the core, respectively, and the third term describes the energy of Coulomb interaction and we have omitted, as usually, the numerical coefficients. Minimization of the free energy, equation (A.1), with respect to Q^* gives the equilibrium value of uncompensated charge of the core:

$$\frac{Q^*}{e} \cong (R/l_B) \ln \left\{ \left(\frac{Q}{Q^*} - 1 \right) \frac{V}{R^3} \right\} \quad (\text{A.2})$$

As follows from equation (A.2), at $Ql_B/(eR) \ll 1$ and $V/R^3 \gg 1$ the fraction of counterions $(Q - Q^*)/Q$ penetrating the core and partially compensating the core charge is small so that the total charge of the core region is equal to the value of an immobilized charge: $Q^* \cong Q$; this is the regime of a strong charge separation.

However, at larger values of the frozen charge Q , when $Ql_B/(eR) \geq 1$, the value of uncompensated charge of the core Q^* weakly increases with an increase in Q . This is due to the re-distribution of counterions which penetrate the core and compensate partially the core charge. Neglecting the logarithmic dependence we can present the solution of equation (A.2) at $Ql_B/(eR) \geq 1$ in the form

$$Q^*/e \cong R/l_B \quad (\text{A.3})$$

At $Ql_B/(eR) \gg 1$ almost all counterions are localized inside the core and only a small fraction of them $Q^*/Q \cong eR/(Ql_B)$ remains free in the outer region of the shell.

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