

Stretching of Polyelectrolyte Coils and Globules in an Elongational Flow

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ABSTRACT: Scaling theory describing the stretching of a weakly charged polyelectrolyte molecule by elongational shear flow is developed. This stretching transition occurs as a first-order dynamic phase transition at a certain "critical" value of the flow-field gradient. The dependence of this critical gradient on the degree of chain ionization and on the solvent strength with respect to the interaction of uncharged monomers is analyzed. The stretching transition in neutral and polyelectrolyte globules is considered. It is shown that for a polyelectrolyte immersed in a salt-added solution two critical values of the flow-field gradient exist: the lower critical point corresponds to the stretching of the chain on the scale of superblobs of the size equal to Debye screening length, and the upper critical point corresponds to the complete stretching of the chain on the scale of monomer units.

1. Introduction

The specific rheological properties of solutions of flexible polymer chains are determined by the ability of polymer coils to be strongly deformed in response to comparatively weak forces applied to a polymer in shear flows.¹ The electrostatic interactions change the unperturbed chain conformation and elasticity so that one can expect different behavior of uncharged and charged polymer molecules in the flows.

It is known¹ that so-called elongational shear flows (flows with longitudinal gradient) affect drastically the conformation of polymer chains immersed in the flow, causing an abrupt coil-stretch transition.

As has been shown,¹⁻⁴ the coil-stretch transition for a neutral polymer molecule occurs as a first-order dynamic phase transition at a certain value of the flow-field gradient. At weak shear the chain retains, in general, an unperturbed coil conformation, whereas at strong shear (exceeding some critical value) the stable conformation corresponds to a completely stretched chain. The critical value of the gradient is determined by the elastic modulus and the friction coefficient of the chain and is inversely proportional to the fundamental relaxation time.

Numerous technological applications of water-soluble polymers (most of which are polyelectrolytes) establish the importance of a theoretical analysis of polyelectrolyte conformations in shear flows.

As the polyelectrolyte chain is partially stretched by the intramolecular Coulomb repulsion of charged monomers, one can expect an additive effect of two stretching forces (electrostatic and hydrodynamic) and, correspondingly, a decrease in the critical flow-field gradient value.

The behavior of a polyelectrolyte macromolecule in an elongational flow was considered by Dunlap et al.⁵ on the basis of a dumbbell model with conformation-dependent elastic and friction coefficients. The polyelectrolyte nature of the chain was taken into account by a Coulomb repulsion between the dumbbell beads possessing an effective charge. It was shown that an

increase in this charge results in a shift of the critical flow-field gradient (corresponding to the coil-stretch transition) to smaller values. This conclusion agrees qualitatively with experimental data for polyelectrolyte solutions in the elongational flow fields created by means of opposite jets or cross-slots⁶ or two- and four-roll mills.⁷

The stretching of the macromolecule was followed by observing the development of the optical birefringence. The theoretical prediction also agrees with experimental results obtained for other examples of flows involving the extensional motion: turbulent pipe flow,⁸ orifice flow,⁹ converging channels,¹⁰ porous media flow.¹¹

In Dunlap's model⁵ the added salt changes only the value of the effective charge. However, as has been shown in ref 12 for weakly charged polyelectrolyte chains without excluded-volume interaction, the coupling between electrostatic and hydrodynamic interactions results in more complicated behavior of a chain in an elongational flow: in the case of a salt-added solution, we predict the existence of two successive stretching transitions. The first of these transitions is from a swollen polyelectrolyte coil to a partially stretched conformation, and the second one is from a partially stretched state to a completely stretched conformation. The physical origin of the stability of the intermediate state is, of course, an increase in the elastic modulus of the swollen polyelectrolyte coil accompanying the polyelectrolyte chain stretching.

The results obtained in ref 12 concern the case of Θ solvent conditions; i.e., excluded-volume interactions between uncharged monomers of the chain were not taken into account. However, for most polyelectrolytes water is a poor solvent for the uncharged backbone of the polyion; i.e., the interaction between uncharged monomer units of the chain has short-range attractive character and can lead to the formation of a polyelectrolyte globule. The stretching of polymer and polyelectrolyte globules by the shear flow should occur at substantially larger flow-field gradients because (i) the size and as a result the friction coefficient of the globule is comparatively small and (ii) the intramolecular attraction must be overcome. Let us note that in

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contrast to neutral polymer globules which have a strong tendency to aggregate a solution of polyelectrolyte globules is stabilized by the Coulomb repulsion between globules that makes possible an experimental observation of their stretching by the shear flow.

In this paper we present a theory of the stretching of weakly charged polyelectrolyte molecules in an elongational flow under the conditions of arbitrary solvent strength including a theory of the stretching of a polyelectrolyte globule. The dependences of the critical flow-field gradient on the solvent strength and on the ionic strength of the solution as well as on the degree of chain ionization are analyzed in scaling terms. After a description of the model of a polyion in an elongational shear flow (section 2), we present the scaling approach used to describe of the coil-stretch transition in neutral polymer coils and extend it to the analysis of the corresponding transition in a polymer globule (section 3). Next we review the main ideas concerning the conformation of a single polyelectrolyte molecule in the bulk of a salt-free solution (section 4). In section 5 we consider the stretching of a polyelectrolyte molecule by the elongational flow in the salt-free solution and estimate the critical values of the flow-field gradient corresponding to the transition between a partially and completely stretched polyion conformation.

The conformations of swollen polyelectrolyte coils and polyelectrolyte globules in a salt-added solution and their stretching by an elongational flow are analyzed in section 6, and the final results are discussed in section 7.

2. Model

Let us consider a long-chain molecule consisting of $N \gg 1$ monomer units and let every m th unit carry an elementary charge e so that the total charge of the polyion is equal to $Q = eN/m$. We assume the following:

(1) The monomer unit length, a , is equal to the Kuhn segment length (flexible backbone of the polyion).

(2) The Bjerrum length $l_B = e^2/T\epsilon$, which characterizes the strength of the Coulomb interaction, is of order a , so that the dimensionless coupling parameter $u = l_B/a \approx 1$; here ϵ is the dielectric constant of the solvent, and T is the temperature in energy units.

(3) The total fraction m^{-1} of charged monomer units in the chain is small: $m^{1/2} \gg u$ so that intramolecular electrostatic interactions do not lead to local chain stiffening.

(4) Nonelectrostatic intramolecular interactions between uncharged monomer units are described by the second, a^3v , and the third, a^6w , virial coefficients. The former depends on the solvent strength (v is positive or negative under good or poor solvent conditions, respectively, and vanishes at the Θ -point), whereas the latter is supposed to be of order unity, $w \approx 1$, independent of the solvent strength.

(5) The solution is so dilute that we can neglect the interactions between different macromolecules.

The condition of total electroneutrality results in the presence of N/m small mobile counterions per polyelectrolyte molecule in the solution. The solution can also contain ions of low molecular weight salt; in the latter case the inverse Debye screening length, κ , is related to the salt concentration n_s via the equation $\kappa^2 \approx l_B n_s$.

We suppose the polyion to be immersed in a stationary elongational flow of the form

$$v_x = sx, \quad v_y = -sy/2, \quad v_z = -sz/2 \quad (1)$$

and to stay in the flow with constant gradient s for a period of time which is many times the characteristic time of the stretching transition.

In the framework of the scaling approach used below we omit all the numerical coefficients and nonpower dependencies.

3. Stretching of a Neutral Polymer Chain in an Elongational Flow Field: Solvent Strength Effects

Following the lines of,^{1,2} we determine the stable conformation of a neutral polymer in the flow on the basis of the analysis of the shape of an effective potential

$$U_{\text{eff}}(R) = F_{\text{Kramers}}(R) + F_{\text{elastic}}(R) \quad (2)$$

which includes two essential contributions dependent on the polymer dimension R :

(1) Kramers potential,^{13,14} whose derivative determines the friction force applied to a polymer in an elongational flow described by eq 1; this force tends to stretch the chain in the x -direction^{13,14}

$$F_{\text{Kramers}}(\alpha)/T \approx -s\tau\alpha^3 \quad (3)$$

where $\alpha = R/(N^{1/2}a)$ is the ratio of the stretched chain dimension to the unperturbed (Gaussian) one, $\tau \approx N^{3/2}a^3\eta/T$ is the fundamental relaxation time of an uncharged chain under Θ solvent conditions,¹ and η is the viscosity of the solvent. The use of the expression (3) for the description of the effect of the flow on the chain means the following: (i) substitution of the three-dimensional flow field (1) by a one-dimensional one; the correctness of such a substitution is discussed elsewhere;² (ii) the friction coefficient of a chain is assumed to be $\zeta \approx \zeta_g\alpha$ where ζ_g is the friction coefficient of a Gaussian chain $\zeta_g \approx \eta N^{1/2}a$. Such an assumption means that we neglect the logarithmic term in the expression for ζ at large extensions.¹⁵

(2) An elastic free energy whose derivative determines the elastic force arising in a deformed polymer and preventing the chain from stretching. This term can be presented in different forms depending on the solvent strength:

$$F_{\text{elastic}}(\alpha, z)/T \approx \begin{cases} \alpha^{5/2} z^{-1/2} \\ \alpha^2 \\ \alpha^{1/2} |z|^{3/2} \end{cases} \quad (4)$$

under the conditions of good, Θ , and poor solvent, respectively. Here $z = N^{1/2}v \approx \text{sign}(v)N^{1/2}a\xi_t^{-1}$ is the conventional parameter characterizing the strength of excluded-volume interactions in the chain, $\xi_t \approx a|v|^{-1}$ is the thermal correlation length (the chain part of size ξ_t remains unperturbed by excluded-volume interactions); $\alpha \approx z^{1/5}$ and $\alpha \approx |z|^{-1/3}$ under the conditions of good and poor solvent, respectively.

Note that under the conditions of good and Θ solvents the elasticity of a swollen or Gaussian coil is determined by the conformational entropy losses under chain stretching. We have omitted in eq 4 the logarithmic term which is irrelevant at large α ; we have also not included a nonlinear term which is significant at strong extensions and takes into account the limited extensibility of a chain. The latter term determines the stretched state of the chain and is irrelevant for present consideration.

Under poor solvent conditions the growth of the elastic free energy under a chain deformation is related to an increase in the surface free energy of the globule under the condition of conservation of the globule's volume and, consequently, the conservation of the volume contribution to the free energy of nonelectrostatic interactions; the corresponding surface tension coefficient is given by $\gamma/T \approx \xi_t^{-2}$ (see refs 21 and 22 for details).

The potential curves $U_{\text{eff}}(\alpha, z)$ exhibit a maximum at

$$\alpha_{\text{max}} \approx \begin{cases} (s\tau)^{-2} z^{-1} \\ (s\tau)^{-1} \\ (s\tau)^{-2/5} |z|^{3/5} \end{cases} \quad (5)$$

The height of this maximum is given, correspondingly, by

$$(U/T)_{\text{max}} \approx \begin{cases} (s\tau)^{-5} z^{-3} \\ (s\tau)^{-2} \\ (s\tau)^{-1/5} |z|^{9/5} \end{cases} \quad (6)$$

It is easy to see that the crossover between (5) and (6) occurs at $(s\tau) \approx |z|^{-1}$. At larger elongations, $\alpha \gg \alpha_{\text{max}}$, the effective potential $U_{\text{eff}}(\alpha, z)$ decreases rapidly due to the growth of the Kramers friction term which is proportional to α^3 . Only at extremely large elongations when $\alpha \approx N^{1/2}$ does the nonlinear elastic term come into play and the potential begins to grow again. The deep minimum appearing on the $U_{\text{eff}}(\alpha)$ curve at $\alpha \approx N^{1/2}$ corresponds to the state of the completely stretched chain, $R \approx Na$. The critical value of the flow-field gradient corresponding to the spinodal transition from the swollen or Gaussian coil conformation to the completely stretched state can be estimated from the condition $(U/T)_{\text{max}} \approx 1$. The stretching of the globule occurs at $(U/T)_{\text{max}} \approx F_{\text{elastic}}(\alpha = \alpha_-)/T$. Finally, one gets

$$s_{\text{crit}} \approx \tau^{-1} \begin{cases} z^{-3/5}, z \gg 1 \\ 1, |z| \ll 1 \\ z^{7/3}, z < 0, |z| \gg 1 \end{cases} \quad (7)$$

The dependence of the critical value of the flow-field gradient on the solvent strength via z corresponding to the cross section 1 of Figure 1 ($w < 1$, quasineutral behavior) is presented in Figure 2, curve 1. As follows from eq 7 and Figure 2, an increase in the solvent strength (in terms of z) leads at $|z| > 1$ to a monotonic decrease in the value of s_{crit} .

Note that eq 7 can be presented also in the form:

$$(s\tau(\alpha))_{\text{crit}} \approx 1 \quad (8)$$

where

$$\tau(\alpha) = \zeta(\alpha)/K(\alpha) \quad (9)$$

is the fundamental relaxation time of a swollen ($\alpha > 1$) or a collapsed ($\alpha < 1$) or Gaussian chain; $\tau(\alpha = 1) \equiv \tau$; the chain friction coefficient is given by

$$\zeta(\alpha) \approx \zeta_g \alpha \quad (10)$$

and the elastic modulus

$$K(\alpha) \approx K_g \frac{\partial^2 F_{\text{elastic}}(\alpha)}{\partial \alpha^2} \quad (11)$$

where $K_g = (Na^2)^{-1}$. Taking into account eqs 4 and 7 and $\alpha(z > 1) \approx z^{1/5}$ and $\alpha(z < -1) \approx |z|^{-1/3}$, we get eq 8.

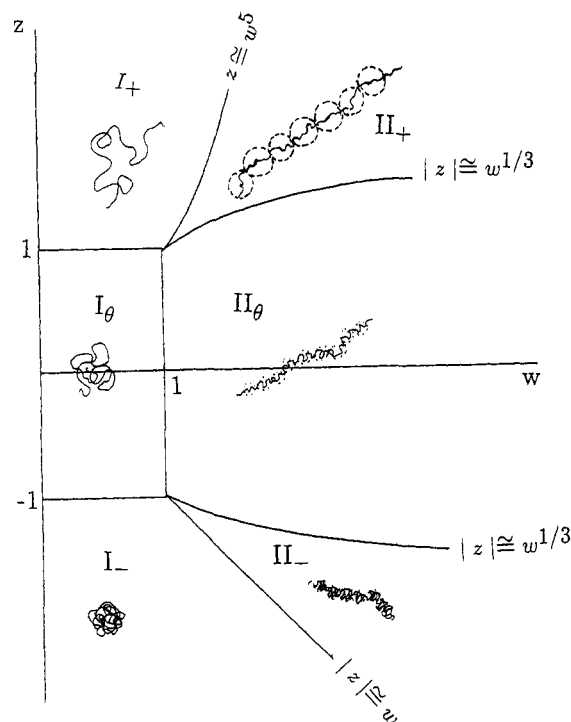


Figure 1. Diagram of states of a polyelectrolyte molecule in a salt-free solution.

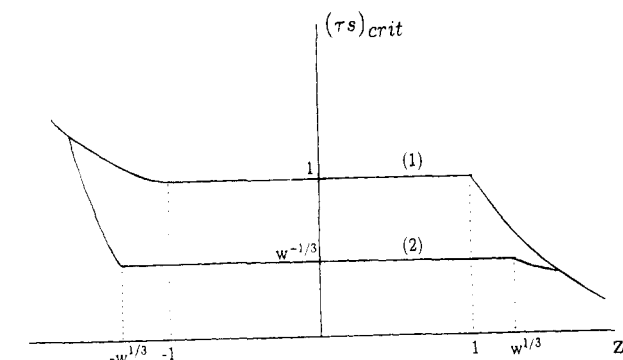
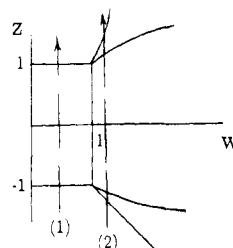


Figure 2. Schematic dependence of the critical value of the flow-field gradient on solvent strength. Curves 1 and 2 correspond to cross sections 1 (quasineutral regime) and 2 (polyelectrolyte regime) of the diagram, respectively.

4. Polyelectrolyte Conformations in a Salt-Free Solution

In this section we review the main ideas concerning the conformation of a polyelectrolyte molecule in the bulk of a salt-free solution without any flow field. In the bulk of a very dilute salt-free solution an individual polyion loses counterions. As a result, the interaction between charged monomers has the character of unscreened Coulomb repulsion. This repulsion strongly affects the polyelectrolyte conformation, causing partial stretching of the chain whose characteristic size becomes proportional to the degree of polymerization

$N^{16,17}$ The equilibrium chain conformation and chain dimension, $R = R_0$, are determined by the condition of a minimum in the free energy

$$F(\alpha) = F_{\text{Coulomb}}(\alpha) + F_{\text{elastic}}(\alpha, z) \quad (12)$$

which includes the elastic free energy $F_{\text{elastic}}(\alpha, z)$ given by eq 4 and the electrostatic free energy of the Coulomb repulsion between charged monomers given by

$$F_{\text{Coulomb}}(\alpha)/T \cong w/\alpha \quad (13)$$

where we have introduced a dimensionless interaction parameter

$$w = Q^2/(TN^{1/2}a\epsilon) \quad (14)$$

equal to the energy (in T units) of electrostatic interaction in a Gaussian coil.

Minimization of the free energy defined by eqs 4, 12, and 13 results in an equilibrium chain dimension determined by the competition between the intramolecular Coulomb repulsion of charged monomer units and an elastic force arising in the deformed polymer coil (under good or Θ solvent conditions) or in a globule (under poor solvent conditions):

$$\alpha_0 = \left\{ \begin{array}{l} w^{2/7} z^{1/7} \\ w^{1/3} \\ w^{2/3} |z|^{-1} \end{array} \right\} \quad (15)$$

The corresponding values of the free energy in the minimum are given by

$$F_0/T \cong \left\{ \begin{array}{l} w^{5/7} z^{-1/7} \\ w^{2/3} \\ w^{1/3} |z| \end{array} \right\} \quad (16)$$

It is easy to be convinced that equilibrium polyion dimensions described by eq 15 are proportional to N regardless of the solvent strength.

In the framework of the blob picture¹ the polyion partially stretched by the intramolecular Coulomb repulsion can be presented as a succession of N_B "electrostatic" blobs of size ξ .^{16,17}

$$R_0 = \alpha_0 N^{1/2} a \cong N_B \xi \quad (17)$$

Under good or Θ solvent conditions the chain part inside every blob retains excluded-volume or Gaussian statistics, respectively, and the energy of electrostatic interactions in the blob is of order T so that they are equivalent to the Pincus stretching blobs⁴ formed by the force of intramolecular electrostatic repulsion. The number of monomer units in the blob, $g = N/N_B$, and the blob size ξ are determined by equations

$$l_B g_+^{2/3} / (\xi_+ m^2) \cong 1, \quad \xi_+ \cong g_+^{3/5} a v^{1/5} \quad (18)$$

or

$$l_B g_\Theta^{2/3} / (\xi_\Theta m^2) \cong 1, \quad \xi_\Theta \cong g_\Theta^{1/2} a \quad (19)$$

respectively.

Under poor solvent conditions (polyelectrolyte globule) the electrostatic blobs are collapsed, $\xi_- \gg \xi_t$; the monomer density inside the blob is equal to the density in an ordinary neutral globule and the blob size is determined from the balance of the excess surface free energy and the energy of electrostatic repulsion inside the blob:¹⁹

$$l_B g_-^{2/3} / (\xi_- m^2) \cong (\xi_- / \xi_t)^2, \quad g_- / \xi_-^3 \cong \xi_t^{-1} \quad (20)$$

As follows from eq 20, $\xi_- \cong \xi_\Theta$. Taking into account eqs 18–20, we can rewrite the equilibrium polyion's dimension, $R_0 = \alpha_0 N^{1/2} a$, in the forms

$$R_0^+ \cong R_0^\Theta (\xi_\Theta / \xi_t)^{1/7}, \quad R_0^- \cong R_0^\Theta (\xi_\Theta / \xi_t)^{-1} \quad (21)$$

where $R_0^\Theta \cong N a^2 / \xi_\Theta$.

The diagram of states of an isolated polyion in a salt-free solution is presented in a universal form in z, w coordinates in Figure 1.

Regions I_+ , I_Θ , and I_- of the diagram correspond to a quasineutral swollen or Gaussian coil or to a polymer globule, respectively. These regions occupy the range of small values of the parameter w or large values of z where electrostatic interactions in the chain are negligibly weak in comparison with short-range excluded-volume interactions of uncharged monomers (in I_+ and I_- regimes) or with a conformational entropy (in I_Θ regime) and as a result are unable to affect the chain conformation.

Regions II_+ , II_Θ , and II_- correspond to a partially stretched chain due to intramolecular Coulomb repulsion or to a chain of electrostatic blobs. These blobs are swollen in the II_+ regime, Gaussian in the II_Θ regime, and collapsed in the II_- regime (polyelectrolyte globule). Note that symmetrical boundaries between $II_\Theta - II_+$ regimes and $II_\Theta - II_-$ regimes correspond to the condition $\xi_\Theta \cong \xi_t$.

5. Stretching of a Polyelectrolyte Chain in a Flow: Salt-Free Solution

Hydrodynamic friction and Coulomb repulsion tend to stretch the chain, whereas chain elasticity opposes this stretching (compare ref 20).

Assume the chain charge is sufficient to provide partial chain stretching due to the intramolecular Coulomb repulsion without a flow ($w > 1$, regimes II of the diagram of states). If now two stretching forces (the intramolecular Coulomb repulsion and the friction force) are applied to the chain, the potential curves $U_{\text{eff}}(\alpha)$ exhibit (at sufficiently large s) two minima: the first one at $\alpha \geq \alpha_0$ (eq 15) with a depth $U_{\text{min}} \cong F_0$ corresponding to a partially stretched state and the second one at $\alpha \cong N^{1/2}$ corresponding to a completely stretched state, and a potential barrier U_{max} at $\alpha \leq \alpha_{\text{max}}$ separating these minima. The condition of disappearance of the potential barrier $U_{\text{max}} \cong F_0$ (or, equivalently, $\alpha_{\text{max}} \cong \alpha_0$) corresponds to a spinodal transition from a partially stretched conformation (a chain of electrostatic blobs) to a completely stretched state. This transition occurs at $s \cong s_{\text{crit}}^{(\text{sf})}$ where

$$s_{\text{crit}}^{(\text{sf})} \cong \tau^{-1} \left\{ \begin{array}{l} w^{-1/7} z^{-4/7}, w^{1/3} < z < w^5 \\ w^{-1/3}, |z| < w^{1/3} \\ w^{-5/3} |z|^4, -w < z < -w^{1/3} \end{array} \right\} \quad (22)$$

whereas if $z > w^5$ or $z < -w$, then eq 7 applies. (Superscript (sf) refers to a salt-free solution). The dependence of the critical flow-field gradient for a polyelectrolyte chain on the solvent strength is presented in Figure 2, curve 2, corresponding to the cross section 2 of the diagram of states. Equation 22 can be written also in the form

$$s_{\text{crit}}^{(\text{sf})} \cong \tau^{-1} w^{-1/3} (\xi_t / \xi_\Theta)^x \quad (23)$$

where $x = 4/7, 0$, and -4 under the conditions of good, Θ and poor solvents, respectively.

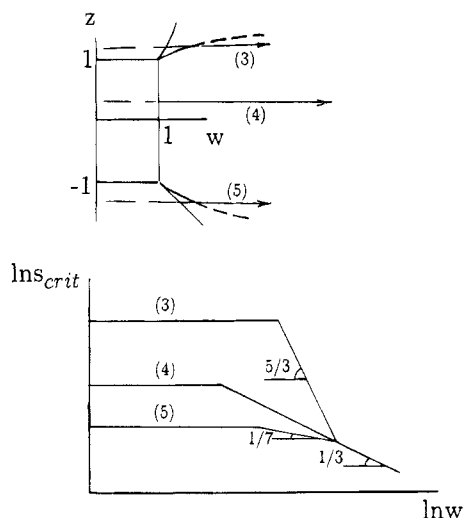


Figure 3. Schematic dependence of the critical value of the flow-field gradient on the polyelectrolyte charge via parameter w under the conditions of good (3), Θ (4), and poor (5) solvents. The corresponding cross sections of the diagram of states are marked by the same numbers.

As follows from eqs 22 and 23, the critical value of the flow-field gradient decreases with an increase in the solvent strength, z , and charge parameter, w . When $w \gg 1$, the critical stretching flow is much weaker for a polyelectrolyte chain than for a neutral one in a wide range of solvent strengths around the Θ -point. The effect is most pronounced for a Θ solvent (weak non-electrostatic interactions), whereas the difference between neutral and polyelectrolyte chains becomes less significant under extremely good or extremely poor solvent conditions. The width of the Θ range increases with w as $w^{1/3}$.

Figure 3 presents the dependence of $s_{\text{crit}}^{(\text{sf})}$ on the parameter w , characterizing the strength of electrostatic interactions in the chain under conditions of good ($z > 1$), Θ ($|z| < 1$), and poor ($z < -1$) solvents corresponding to cross sections 3, 4, and 5 of the diagram of states, respectively. As follows from the Figure 3, the value of $s_{\text{crit}}^{(\text{sf})}$ decreases monotonically with an increase in the chain charge parameter w at large w corresponding to polyelectrolyte regimes $II_{+, \Theta, -}$ of the diagram of states in Figure 1. In the range of small w corresponding to quasineutral regimes $I_{+, \Theta, -}$ the critical gradient remains (in the scaling approximation) virtually independent of w ; this interval of the w value becomes larger as $|z|$ increases.

Note that eq 22 can also be presented in a form $(s\tau(\alpha_0))_{\text{crit}}^{(\text{sf})} \approx 1$ analogous to eq 8, where the fundamental relaxation time of a partially stretched polyelectrolyte is given by eqs 9–11 and 4 at $\alpha = \alpha_0$ given by eq 15.

6. Polyelectrolyte Stretching in a Salt-Added Solution

Let us start from a brief review of the unperturbed by the flow polyelectrolyte conformation in a salt-added solution, supposing that the values of z and w correspond to regions II of the diagram of states (Figure 1), where unscreened intramolecular Coulomb repulsion predominates on a large scale over excluded-volume interactions.

At low salt concentrations, when the Debye screening length κ^{-1} exceeds by far the size R_0 of a polyion in a salt-free solution, the chain conformation and behavior

in the flow remain the same as in a salt-free solution (section 5) (Figure 4a).

In the intermediate range of salt concentrations, $\xi < \kappa^{-1} < R_0$, the chain conformation on scales smaller than κ^{-1} is still determined by unscreened Coulomb repulsion and coincides with that of the polyion in a salt-free solution, whereas the interaction between the parts of the chain of size κ^{-1} can be described as a short-range repulsion with an effective excluded volume of order κ^{-3} .¹⁸ The dimension of a polyion in this regime is given by

$$R_s \approx R_0^{3/5} \kappa^{-2/5} \quad (24)$$

where R_0 is still given by eqs 15, 17, or 21. This conformation may be characterized as a "swollen polyelectrolyte coil" (Figure 4b). Note that locally (on the scale of electrostatic blobs) the chain obeys excluded-volume or Gaussian statistics or even can be collapsed (under poor solvent conditions).

The elasticity of a swollen polyelectrolyte coil depends on the scale of deformation: at comparatively weak elongation, $R_s < R < R_0$, the deformation of the chain occurs on the scale larger than κ^{-1} so that the local blob structure (electrostatic blobs) remains unperturbed. An increase in the free energy related to a weak deformation of a swollen polyelectrolyte coil can be presented as

$$F_{\text{elastic}}(\alpha)/T \approx (\alpha/\alpha_s)^{5/2} \quad (25)$$

where $\alpha_s = R_s/(N^{1/2}a)$.

Equation 25 describes an increase in the conformational free energy of a stretched chain consisting of symmetrical subunits of size κ^{-1} with an excluded volume κ^{-3} . Hence, it takes into account a decrease in the conformational entropy of the backbone of a polyion and a decrease in the energy of screened intramolecular electrostatic repulsion.

At stronger elongations, $R_0 < R < Na$, the elastic free energy $F_{\text{elastic}}(\alpha)$ is given by eq 4.

The critical value of the flow-field gradient corresponding to the stretching of a swollen polyelectrolyte coil by the flow can be obtained from the condition $(s\tau(\alpha_s))_{\text{crit}}^{(s)} \approx 1$, where $\tau(\alpha_s) = \zeta(\alpha_s)/K(\alpha_s)$. Using eqs 10, 11, and 25 at $\alpha = \alpha_s$ one gets $s_{\text{crit}}^{(s)} \approx \tau\alpha_s^{-3}$, or taking into account eqs 15 and 25

$$s_{\text{crit}}^{(s)} \approx \tau^{-1} (N^{1/2} \kappa \alpha)^{6/5} \left\{ \begin{array}{l} w^{-18/35} z^{-9/35} \\ w^{-3/5} \\ w^{-6/5} |z|^{9/5} \end{array} \right\} \quad (26)$$

under the conditions of good, Θ , and poor solvents (swollen, Gaussian, or collapsed electrostatic blobs), respectively. (Superscript (s) refers to a salt-added solution.)

Equation 26 gives the critical value of the flow-field gradient corresponding to the spinodal transition from the swollen coil of superblobs of size κ^{-1} to a completely stretched chain of swollen, Gaussian, or collapsed electrostatic blobs.

The latter conformation coincides, in general, with the conformation of a polyion in a salt-free solution without a hydrodynamic stretching force. As follows from eq 26, the critical value of the flow-field gradient corresponding to the stretching of swollen polyelectrolyte coil decreases with an increase in the solvent strength (z) and in the polyion charge (w). It grows with an increase in the

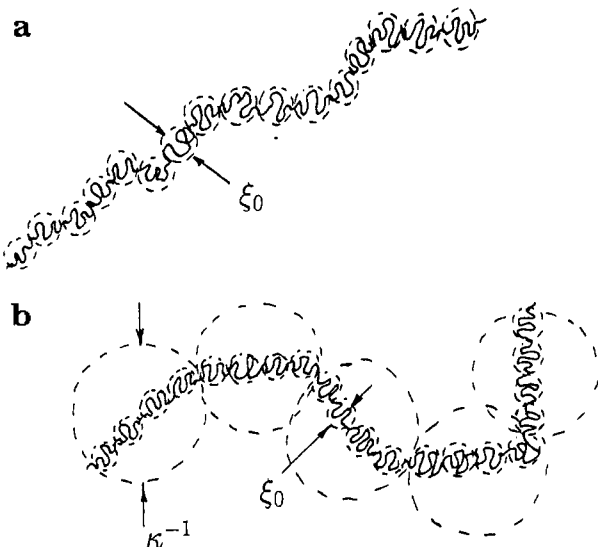


Figure 4. Polyelectrolyte molecule partially stretched in the salt-free solution (a) and swollen in the salt-added solution (b).

ionic strength of a solution as $\kappa^{6/5}$ regardless of the solvent strength.

As follows from the analysis of eqs 22 and 26 at moderate screening (moderate ionic strength of a solution), the range $s_{\text{crit}}^{(s)} < s < s_{\text{crit}}^{(sf)}$ of the flow-field gradient exists. In this range the conformation of a stretched chain of electrolytic blobs remains stable. Thus, at moderate screening two successive transitions occur as the flow-field gradient, s , increases: the first one (at $s \approx s_{\text{crit}}^{(s)}$ defined by eq 26) is the transition from a swollen polyelectrolyte coil to a stretched chain of electrostatic blobs, and the second one (at $s \approx s_{\text{crit}}^{(sf)}$ defined by eq 22) is the transition from a completely stretched chain of electrostatic blobs to a completely stretched chain of monomers. The range of the ionic strength corresponding to the manifestation of two successive stretching transitions is determined by the condition $s_{\text{crit}}^{(s)} < s_{\text{crit}}^{(sf)}$, or taking into account eqs 22 and 26,

$$1 < \kappa R_0 < \begin{cases} w^{25/42} z^{-5/42} \\ w^{5/9} \\ w^{5/18} |z|^{5/6} \end{cases} \quad (27)$$

As can be seen from eq 27, the width of this range depends on the number of chain segments N , distance between charged segments m , and the solvnet strength v as:

$$\begin{aligned} N^{1/6} m^{13/21} v^{1/7} &< (\kappa a)^{-1} < N m^{-4/7} v^{1/7} \\ N^{1/6} m^{4/9} &< (\kappa a)^{-1} < N m^{-2/3} \\ N^{1/6} m^{-4/3} |v|^{-1} &< (\kappa a)^{-1} < N m^{-4/3} |v|^{-1} \end{aligned} \quad (28)$$

under good, Θ , and poor solvent conditions, respectively. As follows from inequalities (28), the two-step transition can be observed only if the macromolecules are sufficiently long (at $m \sim 10$, $N > 10^3$). At larger salt concentration when inequality (27) is violated, the value of s required for stretching of a swollen polyelectrolyte coil becomes large enough. The state of a completely stretched chain of electrostatic blobs becomes unstable at $s > s_{\text{crit}}^{(s)}$, and the polyion acquires a completely stretched conformation as a result of the one-stage stretching transition. It is easy to prove that the finite

range of salt concentration corresponding to the two-stage stretching transition always exists for w, z corresponding to regions II of the diagram of states (Figure 1).

Further increase in the ionic strength of a solution results at $\kappa^{-1} < \xi$ in the screening of electrostatic interactions on the scale smaller than the electrostatic blob size ξ .

Under the conditions of good solvent (swollen electrostatic blobs, region II₊ of the diagram in Figure 1) the polyelectrolyte chain acquires at $\kappa^{-1} < \xi_+$ the conformation of a quasineutral swollen coil in which nonelectrostatic excluded volume interaction between uncharged monomers predominates over Coulomb interaction and determines the chain conformation. The value of the critical flow-field gradient s_{crit} required for the stretching of the chain is given by eq 7.1.

Under poor solvent conditions (collapsed electrostatic blobs, region II₋ of the diagram in Figure 1) the chain conformation at $\kappa^{-1} < \xi_-$ coincides with the conformation of an ordinary polymer globule and is determined by the balance between binary attraction and ternary repulsion of uncharged monomers; the corresponding critical value of the flow-field gradient is given by eq 7.3.

Finally, under Θ solvent conditions (Gaussian electrostatic blobs, region II _{Θ} of the diagram in Figure 1) the polyelectrolyte chain acquires at $\kappa^{-1} < \xi_\Theta$ the conformation of a swollen coil, but the swelling is determined by screened Coulomb repulsion between charged monomers; the value of an effective second virial coefficient is given by $v_{\text{eff}} \approx m^{-2} l_{BK}^{-2}$. The coil size and the critical flow-field gradient in this case are given by eqs 24 and 26.2, respectively. Further increase in a salt concentration (in κ) results in a decrease in v_{eff} and at $v_{\text{eff}} \leq |v|$ the chain passes into one of the quasineutral regimes: a swollen coil at $z > 1$, a globule at $z < -1$, or a Gaussian coil at $|z| < 1$; the corresponding values of s_{crit} are given by eq 15 with $z_{\text{eff}} = (v + v_{\text{eff}})N^{1/2}$.

7. Conclusion

In the present paper we have analyzed in scaling terms the influence of the intramolecular Coulomb and excluded-volume interactions on the behavior of a polyelectrolyte molecule in an extensional flow field. The interplay between three main parameters, w, z , and s , characterizing the magnitude of the Coulomb, osmotic (excluded volume), and hydrodynamic friction force, respectively, determines the stability of different conformations of a polyelectrolyte molecule in the flow.

As has been shown, at small and moderate values of the flow-field gradient, s , the local conformational structure of the macromolecule is determined by short-range excluded-volume interactions: the polyelectrolyte chain can be presented as a chain of swollen, Gaussian, or collapsed electrostatic blobs. If the electrostatic screening length is much smaller than the overall dimension of the polyion and the hydrodynamic stretching force is weak (s is small), the chain of blobs acquires the conformation of a coil swollen by screened Coulomb repulsion between blobs. At weak electrostatic screening or sufficiently large s , the chain of blobs becomes stretched due to long-range intramolecular Coulomb repulsion or due to the hydrodynamic stretching force, respectively. The latter conformation corresponds to a partial stretching of the polyion's backbone.

Further stretching is related to the rearrangement of the chain conformation on the scale of electrostatic blobs. The elastic response of the chain to this deformation appears to be much stronger than the response to large-scale deformation. As a result, the conformation of a partially stretched chain (completely stretched chain of blobs) remains stable in a certain range of the flow-field gradient in a salt-added solution.

Thus, we predicted a qualitative difference in the coil-stretching transition induced by the elongational shear flow in weakly charged polyelectrolytes in a salt-added solution and in neutral chains: a two-stage transition is expected in the former case in contrast to the one-stage transition in the latter case. In both cases the transition has the character of a dynamic first-order phase transition.

The critical values of the flow-field gradient appear to be strongly dependent on the degree of chain ionization and on the salt concentration (eqs 22 and 26). These power dependencies can be checked in the experiments on polyelectrolyte stretching in the elongational flow if the degree of chain ionization and the ionic strength of a solution are varied. Let us mention, however, that all the equations obtained above refer to quenched polyelectrolytes (with a conformationally independent degree of ionization). For so-called annealed polyelectrolytes (weak polybases or polyacids, for instance) the degree of ionization depends on the local concentration of counterions. As a result the stretching of annealed polyelectrolytes can be accompanied by the variation of the chain charge. So far we have not taken this effect into account.

Let us note that our analysis makes it possible to determine the range of stability of different chain conformations: spinodals rather than binodals corresponding to the dynamic phase transitions are obtained. This is meaningful from the experimental point of view, because the time spent by a macromolecule in the region of the stretching flow field is always limited by experimental conditions.

The range of validity of the theory is restricted by the dilute solution conditions (a single-chain approximation has been used above). More complicated effects arising in a semidilute solution are related to the screening of both Coulomb and hydrodynamic interactions due to the presence of other polyelectrolyte chains and their counterions. These effects will be considered in a forthcoming paper.

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List of Symbols

$\alpha = R/(N^{1/2}a)$	reduced dimension of a polyelectrolyte chain, in particular α_0 and α_s
α_0	in the absence of the flow in a salt-free solution
α_s	in the absence of the flow in a salt-added solution

ϵ	dielectric constant of the solvent
ζ	friction coefficient of a polyelectrolyte molecule
ζ_g	friction coefficient of a Gaussian coil
η	viscosity of a solvent
κ	inverse Debye screening length
ξ	electrostatic blob size, in particular ξ_0 and ξ_-
ξ_0	under Θ solvent conditions
ξ_+	under good solvent conditions
ξ_t	thermal correlation length
$\tau(\alpha)$	fundamental relaxation time of the chain
$\tau \approx N^{3/2}a^3\eta/T$	fundamental relaxation time of a Gaussian coil
a	monomer length
e	electron charge
F_{Coulomb}	free energy of intramolecular Coulomb repulsion
F_{elastic}	elastic free energy of chain deformation
F_{Kramers}	Kramers potential
F_0	free energy of a polyion stretched by intramolecular Coulomb force
g	number of monomers in an electrostatic blob, in particular g_+ and $g_{0,-}$ under the conditions of good, Θ or poor solvent, respectively
$K(\alpha)$	elastic modulus
K_g	elastic modulus of a Gaussian coil
$l_B = e^2/\epsilon T$	the Bjerrum length
N	number of monomers in the chain
N/m	number of charged monomers in the chain
Q	total charge of the chain
R_0	equilibrium dimension of a polyelectrolyte chain in a salt-free solution in the absence of the flow, in particular R_0^+ and $R_0^{\Theta,-}$
R_0^+	under the conditions of good solvent
$R_0^{\Theta,-}$	under the conditions of Θ or poor solvent, respectively
R_s	equilibrium size of a polyelectrolyte chain in a salt-added solution
s	flow-field gradient
s_{crit}	critical value of the flow-field gradient corresponding to the stretching transition in a neutral chain
$s_{\text{crit}}^{(\text{sf})}$	the same for a polyelectrolyte chain in a salt-free solution
$s_{\text{crit}}^{(s)}$	the same for a polyelectrolyte chain in a salt-added solution
T	temperature in energy units
$\{v_x, v_y, v_z\}$	components of the flow velocity field
va^3	the second virial coefficient of the interaction of uncharged monomers
wa^6	the third virial coefficient of the interaction of uncharged monomers
$v_{\text{eff}} \approx m^{-2}l_B\kappa^{-2}$	effective electrostatic second virial coefficient
$w \approx Q^2/(N^{1/2}a\epsilon T)$	parameter of electrostatic intramolecular interaction
$z \approx vN^{1/2}$	parameter of excluded-volume intramolecular interaction

References and Notes

- (1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (2) de Gennes, P.-G. *J. Chem. Phys.* **1974**, *60*, 5030.

- (3) Hinch, E. J. *Phys. Fluids* **1977**, *20*, S22.
- (4) Pincus, P. *Macromolecules* **1977**, *10*, 210.
- (5) Dunlap, P. N.; Leal, L. G. *Rheol. Acta* **1984**, *23*, 283.
- (6) Miles, M. J.; Tanaka, K.; Keller, A. *Polymer* **1983**, *24*, 1082.
- (7) Dunlap, P. N.; Wang, C.-H.; Leal, L. G. *J. Polym. Sci., B: Polym. Phys.* **1987**, *25*, 2211.
- (8) Virk, P. S. *Nature* **1975**, *253*, 109.
- (9) Ouibrahim, A.; Fruman, D. H. *J. Non-Newtonian Fluid Mech.* **1980**, *7*, 315.
- (10) Merrill, E. W.; Horn, A. F. *Polym. Commun.* **1984**, *25*, 144.
- (11) Durst, F.; Haas, R.; Interthal, W. *Rheol. Acta* **1982**, *21*, 572.
- (12) Darinskii, A. A.; Borisov, O. V. *Europhys. Lett.* **1995**, *29*, 365.
- (13) Rabin, Y.; Henyey, F. S.; Pathria, R. K. *Phys. Rev. Lett.* **1985**, *55*, 201.
- (14) Kramers, H. A. *J. Chem. Phys.* **1946**, *14*, 415.
- (15) Brestkin, Yu. V.; Gotlib, Yu. Ya.; Klushin, L. I. *Polymer Sci. USSR* **1989**, *31*, 1143.
- (16) de Gennes, P.-G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. Fr.* **1976**, *37*, 1461.
- (17) Khokhlov, A. R.; Khachaturian, K. A. *Polymer* **1982**, *23*, 1742.
- (18) Barrat, J.-L.; Joanny, J.-F. *Europhys. Lett.* **1993**, *24*, 333.
- (19) Khokhlov, A. R. *J. Phys. A* **1980**, *13*, 979.
- (20) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *J. Phys. II* **1994**, *4*, 913.
- (21) Halperin, A.; Zhulina, E. B. *Europhys. Lett.* **1991**, *15*, 417.
- (22) Halperin, A.; Zhulina, E. B. *Macromolecules* **1991**, *24*, 5393; *Vysokomol. Soedin.* **1989**, *31A*, 1143.

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