Macromol. Symp. **2009**, 278, 24–31

DOI: 10.1002/masy.200950404

Effect of the Ionic Strength on Collapse Transition in Star-like Polyelectrolytes

Alexey A. Polotsky,[*1] *Ekaterina B. Zhulina,*[1] *Tatiana M. Birshtein,*[1] *Oleg V. Borisov*[1,2]

Summary: We present an analytical theory describing intramolecular conformational transition in a star-shaped polyelectrolyte (PE) molecule induced by a decrease in the solvent strength or/and increase in the ionic strength in the solution. We apply a mean-field Flory-type analysis in a box-like approximation, that is we assume fairly uniform distribution of densities of charged monomer units and all mobile ions (co- and counterions) in the intra-molecular volume of the star. We demonstrate that depending on the number of branches, fraction of charged monomers in the star and the ionic strength of the solution different scenario of the collapse transition may take place. At high ionic strength or low degree of ionization collapse transition occurs continuously resembling the collapse of a neutral polymer star.[1] On the contrary, at low ionic strength and high degree of ionization collapse transition features first order phase transition, that is, occurs discontinuously and involves coexistence of collapsed and stretched states.

Keywords: box-like model; collapse transition; polyelectrolyte star; theory

Introduction

Ionic polymers, or polyelectrolytes (PEs), find many technological applications, from oil recovery (rheology control) to nanomedicine (gene delivery). Both experimental and theoretical studies aim to understand the conformational properties of polyelectrolytes in aqueous solutions. The stimuli-responsive properties of polyelectrolytes, i.e., the ability to respond by conformational changes to variations in environmental conditions, e.g., in the ionic strength of the solution, are of key importance for many applications.

Recent progress in controlled radical polymerization (CRP) has made it possible to synthesize star-like polyelectrolytes with well-controlled number of arms and degree of polymerization by exploiting so-called ''core-first'' approach, which assumes use of oligo-functionalized initiators for CRP.[2–5] Obtained regular star-shaped polyelectrolytes present excellent model systems for experimental studies aiming at unraveling of essential features arising because of branched topology of such ionic macromolecules. Furthermore, complexes of the star polyelectrolytes with the oppositely charged ionic macromolecules are explored experimentally as promising candidates for non-viral gene vectors.[6]

The most distinctive feature of star-branched polyelectrolytes is localization of mobile counterions in the intra-molecular volume of the PE star.[7–9] The effect of the counterion localization is most pronounced in salt-free solutions of the many-arm stars. Here strong electrostatic potential created by branched macroion attracts the counterions, which get preferentially localized in the interior volume of the star thus almost compensating its charge and create strong

---

[1] Institute of Macromolecular Compounds, Russian Academy of Sciences 31 Bolshoy pr., 199004 St.-Petersburg, Russia
E-mail: alexey.polotsky@gmail.com

[2] Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (IPREM) CNRS/UPPA, Pau, France

excess osmotic pressure. The effect of the counterion localization has been proven by exact Poisson-Boltzmann analysis [8,10,11] as well as by Monte Carlo[12] and molecular dynamics[13,14] simulations. This osmotic pressure of entrapped counterions induces swelling of the PE star and radial extension of the branches.

The intramolecular collapse transition induced in salt free solution of PE stars by a decrease in the solvent strength has been considered by Borisov et al [15] and by Ross and Pincus [16] on the basis of local electroneutrality approximation within the simplified box-like model, which assumes fairly uniform concentration of monomer units inside the star and local compensation of charge density of ionic monomer units by that of mobile counterions. This analysis proved that in contrast to progressive collapse of a neutral star,[1] the collapse of a PE star features first order phase transition and involves (at certain solvent strength significantly below the theta-point) co-existence of collapse and swollen stars. Later Misra et al [17] suggested, that the micro-phase coexistence between collapsed and swollen phases may occur inside an individual PE star.

The main objective of the present paper is to analyse collapse transition provoked in PE stars by decrease in the solvent strength and particularly to consider the effect of the ionic strength of the solution on the character of the collapse transition and on the transition point. Our present analysis is limited to strongly dissociating PE stars, whose degree of ionisation is virtually independent of pH and ionic strength in the solution. A detailed study of the collapse transition in the pH sensitive PE stars and analysis of the effetcs of coupling between confirmations and degree of ionisation of branches will be a matter of future publication. In our analysis we exploit the box-like model thus neglecting non-uniform radial distribution of densities of all the components. This model, however, enables us to go beyond the local electroneutrality approximation and to consider combined effects of osmotic pressure of counterions and electrostatic repulsion of charged arms on the swelling-to-collapse transition in PE stars.

Model and Free Energy

Consider a polymer star with p arms each consisting of N spherically symmetric monomer units of the size a, Figure 1.

The fraction α of the monomer units are permanently (negatively) charged with the elementary charge $-e$ and we assume that the condition of weak charging, $\alpha \ll (l_B/a)^2 \cong 1$, where $l_B = e^2/\varepsilon k_B T$ is the Bjerrum length, is fulfilled. The star is immersed into a polar solvent (water) containing monovalent salt (1:1 electrolyte) with concentration c_s, which determines the Debye screening length $r_D = (8\pi l_B c_s)^{-1/2}$.

In our present analysis we apply the box-like approximation, that is, neglect gradients in local polymer density in the radial direction and assume uniform stretching of the arms. In the box-like approximation the star is characterized by average intramolecular concentration of monomer units

$$c = \frac{3pN}{4\pi R^3} \tag{1}$$

The box-like approximation together with the local electroneutrality approximation has been used for analysis of the

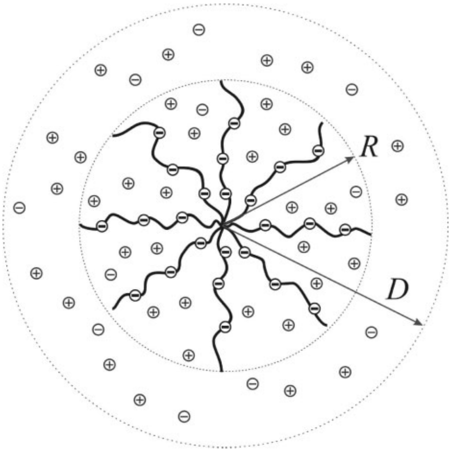

Figure 1.
Polyelectrolyte star.

collapse-to-swelling transitions in neutral polymer star[1] and in quenched PE stars without salt.[15] Although the box-like model does not provide a detailed picture of evolution of the interior structure of the star (i.e. radial distribution of the monomer units density) upon the collapse transition, it enables to capture the character of the transition and to analyze the transition point as a function of the interaction and the molecular architecture parameters.

In contrast to previous studies of the collapse transition in PE stars, for our present analysis we apply the box-like model without pre-assumption of the electroneutrality (charge compensation) of the intramolecular volume of the star. Similarly, in refs.,[8,10] conformation of the star like PE in good and theta solvents and partitioning of counterions between intramolecular and external volumes have been analyzed in the framework of the cell model: the PE star was considered as localized in the center of the electroneutral as a whole (containing also all the counterions) spherical cell. The size of the spherical cell available for counterions corresponded to the average inter-star distance in the solution which depend on the PE stars' concentration. This approach has made it possible to analyze concentrational effects on the PE star conformations in good and theta-solvent.

For the purposes of analysis of the effect of added electrolyte on the PE star conformation and collapse transition we apply similar approach, but the size $D \geq R$ of the minimal electroneutral cell (Figure 1) should be determined from minimization of the free energy of the cell coupled to the reservoir of solvent with fixed chemical potentials of all mobile ion species:

$$F(R,D) = F_{conf}(R) + F_{int}(R) + F_{ions}(D) + F_{Coulomb}(R,D) \qquad (2)$$

which comprises

- conformational free energy of the star arms approximated as that of the uniformly stretched Gaussian chain

$$F_{conf}(R)/k_BT = p \cdot \frac{3R^2}{2Na^2} = \frac{3p}{2Na^2}\left(\frac{3Np}{4\pi c}\right)^{2/3} \qquad (3)$$

(we remind the reader, that the latter expression is applicable as long as the arms remain stretched with respect to the Gaussian chain dimensions, $R \geq N^{1/2}a$, that might be not the case under very poor solvent strength conditions; the corrected elastic term has been implemented in ref.[1] for analysis of collapse of neutral stars; apparently for analysis of transition in PE stars, which are strongly stretched by osmotic pressure of counterions, Eq. (3) provides a satisfactory accuracy);

- the free energy of short-range non-electrostatic (excluded volume) interactions within the star which can be represented via virial expansion

$$F_{int}(R)/k_BT = pN(\upsilon c + wc^2), \qquad (4)$$

where υ and w are the second and the third virial coefficients of the interaction of the monomer units, respectively. Variation in the solvent strength corresponds to variation of the second virial coefficient, υ, which is positive under good solvent conditions, negative in poor solvent and vanishes in the theta-point;

- the contribution describing translational entropy of mobile co- and counterions which is given by

$$F_{ions}(D)/k_BT = N_+(\ln c_+ - 1) + N_-(\ln c_- - 1) - (N_+ + N_-)\ln c_s + \frac{8\pi}{3}D^3 c_s \qquad (5)$$

where c_+ and c_- are average concentration of positively and negatively charged ions within the volume of the electroneutral cell of radius D and

$$N_+ = \frac{4\pi}{3}D^3 c_+$$

and

$$N_- = \frac{4\pi}{3} D^3 c_-$$

are the total numbers of positively and negatively charged mobile ions in the cell of radius D. We remark that Eq. (5) assumes uniform distribution of both types of mobile ions in the cell of radius D.

The condition of total electroneutrality of the cell implies

$$p\alpha N + N_- = N_+$$

and together with the Donnan equilibrium condition

$$c_+ \cdot c_- = c_s^2$$

it enables us to determine the concentrations c_+ and c_- of positively and negatively charged ions in the cell:

$$c_\pm = c_s \left[\pm \frac{3\alpha pN}{8\pi D^3 c_s} + \sqrt{1 + \left(\frac{3\alpha pN}{8\pi D^3 c_s} \right)^2} \right]$$

Assuming a uniform distribution of the charged monomer units of the star within the radius R, as well as uniform distribution of both types of mobile ions within the radius D the Coulomb contribution to the free energy can be presented as

$$F_{Coulomb}(R, D)/k_B T = \frac{3}{10} \cdot l_B \cdot \frac{(\alpha pN)^2}{R} \left(\frac{R}{D} + 2 \right) \left(\frac{R}{D} - 1 \right)^2 \tag{6}$$

Diagram of States of a PE Star

Minimization of the free energy $F_{ion}(D) + F_{Coulomb}(R,D)$ with respect to D leads to the equation for the equilibrium radius D of the minimal electroneutral cell,

$$(D^2 - H^2) \left[1 + \sqrt{1 + \frac{9 l_B^2 (\alpha pN)^2 r_D^4}{D^6}} \right] = 10 r_D^2 \tag{7}$$

where $r_D^2 = (8\pi l_B c_s)^{-1}$ is the Debye screening length.

The approximate solutions for D in the corresponding asymptotic regions are presented in Figure 2. The net contribution to the free energy, $F_{ion} + F_{Coulomb}$, arising from translational entropy of small ions and Coulomb interaction of charges is dominated either by the first or by the second term in different regions of the diagram of states presented in Figure 2.

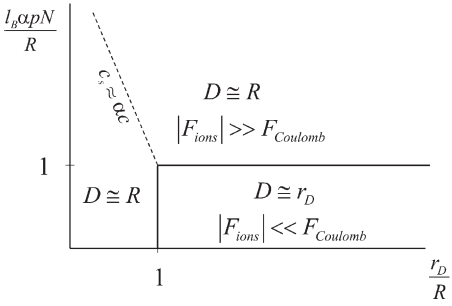

Figure 2.
Diagram of states of polyelectrolyte star.

In the regions of the diagram, where $D \approx R$, that is the case for the star with large number of arms, or/and at large salt concentration, the contribution of the translational entropy of the mobile ions

$$F_{ions}/k_B T \approx \alpha pN \left(\frac{1 - \sqrt{1 + (\alpha c/2c_s)2}}{\alpha c/2c_s} + \operatorname{arsinh}(\alpha c/2c_s) \right), \; R \approx D \tag{8}$$

is the dominant one; the latter expression has two asymptotic limits:

$$F_{ion}/k_B T \approx \begin{cases} \alpha pN \left[\ln \frac{\alpha c}{c_s} - 1 \right], & \alpha c \gg c_s \\ pNc \cdot \frac{\alpha^2}{4c_s}, & \alpha c \ll c_s \end{cases} \tag{9}$$

which correspond to the so-called osmotic and salt dominance asymptotic regimes, respectively.

On the contrary, for stars with small number of arms at low salt concentration $D \cong r_D >> R$ and the Coulomb repulsion provides larger contribution to the free energy than translational entropy of ions;

here

$$F_{Coulomb})/k_BT \approx \frac{3}{5} \cdot l_B \cdot \frac{(\alpha pN)^2}{R}, \qquad R \ll D \cong r_D \tag{10}$$

Collapse-to-swelling Transition

The equilibrium star dimension R or the average intramolecular concentration (see Eq. (1)) is determined from the condition of minimum of the free energy

$$\frac{dF(c)}{dc} = 0$$

that is equivalent to the requirement of vanishing differential osmotic pressure between intramolecular volume of the star and the surrounding solution.

Below we consider separately two limiting cases of stars where dominant contribution to the free energy is provided either by differential osmotic pressure of counterions (osmotic or salt dominance regimes) or by unscreened Coulomb repulsion between charged monomer units.

Osmotic and Salt Dominated Regimes

The free energy minimization results in the the following equation for equilibrium polymer concentration c

$$-\frac{{c_\theta}^{8/3}}{c^{5/3}} + (-\tau + c) + \frac{c_s}{wc^2}\left\{\sqrt{1 + \left(\frac{\alpha c}{2c_s}\right)^2} - 1\right\} = 0 \tag{11}$$

where we have introduced $\tau = -v/2w$ which is the monomer units concentration in a neutral polymer globule in the volume approximation and

$$c_\theta = \frac{3^{1/4}}{2^{7/8}\pi^{1/4}} \cdot \frac{p^{1/4}}{N^{1/2}w^{3/8}}$$

is the equilibrium average concentration of the monomer units in a neutral star under theta-solvent condition, that is at $\alpha = 0$, $\tau = v = 0$.

For analysis of Eq. (11) we introduce reduced variables

$$\eta = c_\theta/c = (R/R_\theta)^3$$
$$t = \tau/c_\theta$$

Then in the case of a neutral star, $\alpha \equiv 0$, Eq. (11) reduces to

$$\eta^{8/3} + t\eta = 1 \tag{12}$$

which is equivalent to that obtained in ref. [1] and describes monotonic decrease in η, that is, in the star size as a function of reduced solvent strength t.

It is instructive to consider first the salt-free limit, $c_s = 0$ studied also earlier in ref. [15]. Here Eq. (11) reduces to

$$\eta^{8/3} + t\eta - a\eta^2 = 1 \tag{13}$$

where

$$\alpha = \frac{\alpha}{2wc_\theta^2}$$

At $t = 0$ and $a \gg 1$ Eq. (13) gives the value of the monomer units concentration in the star in the theta-point, when swelling is exclusively controlled by osmotic pressure of counterions, $c_{osm} = c_\theta^4(2w/\alpha)^{3/2}$.

Analysis of Eq. (13) indicates, that $\eta(t)$ is a single-valued function, that is, $t(c)$ is monotonic if $a \leq a_{crit}$ where

$$a_{crit} = 4.5^{3/4}/3^{3/2}$$
$$\eta_{crit} = (9/5)^{3/8}$$

The star size decreases monotonically as a function of τ, remaining slightly larger than those for a neutral star, but the deviation becomes progressively less important when the star passes into collapsed regime (large t) where the density is primarily controlled by balance of non-electrostatic binary attractive and ternary repulsive interactions, $c \cong \tau$. The critical value of a_{crit} is found from the condition

$$dt(\eta)/d\eta = d^2t(\eta)/d\eta^2 = 0. \tag{14}$$

At $a \geq a_{crit}$, (the latter condition is equivalent to $c_{osm} \leq c_\theta$), that is the case at, e.g., sufficiently high degree of ionization α, the function $t(c)$ exhibits non-monotonic behaviour in the intermediate range of concentration. This indicates a jump-wise transition and possibility of co-existence between collapsed and swollen stars at certain value of $\tau = \tau_{tr}$. The latter should be determined from the condition of equality of the free energy in coexisting collapsed and swollen states. An estimate for the transition point (binodal) is obtained by accounting only the dominant, interaction terms in the free energy of the collapsed state and only counterion entropy together with the elastic term for the swollen state. The result is

$$\tau_{tr}^2 = \frac{\alpha}{w} \cdot \ln\left(\frac{\tau_{tr}}{c_{osm}}\right) - \frac{3c_\theta^{8/3}}{c_{osm}^{2/3}} \approx \frac{\alpha}{w} \cdot \ln \frac{4\pi N^2 \alpha^{2/3} \tau_{tr}}{3p} \tag{15}$$

The difference in concentration of the monomer units in co-existing collapsed and swollen conformations, $\Delta c_{tr} \approx \tau_{tr} - c_{osm}$ increases as a function of α.

Finally, in the general case of of added salt by using reduced variables, Eq. (11) can be represented as

$$\eta^{8/3} + t\eta - \frac{a\eta^3}{s}\left[\sqrt{1+\left(\frac{s}{\eta}\right)^2} - 1\right] = 1 \tag{16}$$

where

$s = \alpha c_\theta / 4c_s$

In the limiting case of $c_s \to 0$ Eq. (16) is reduced to Eq. (13) describing salt-free case. In the opposite limit $s/\eta \ll 1$ or, that is the same $\alpha c/c_s \ll 1$ (so called salt dominance regime) Eq. (16) is reduced to Eq. (12) for neutral star, but with renormalized solvent strength parameter $t \to t - \alpha^2/4c_s c_\theta$. Hence, at high salt concentration the collapse of a PE star occurs continuously, as for the neutral one, but the collapse curve is shifted toward poorer solvent strength conditions by the value of effective electrostatic excluded volume $v_{eff} = \alpha^2/4c_s$.

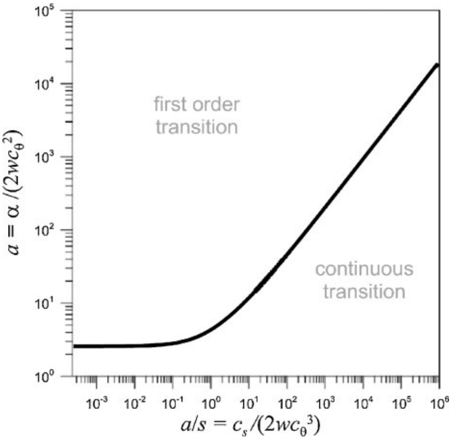

Figure 3.
Phase diagram of quenched polyelectrolyte star in osmotic and salt dominance regimes.

Applying condition (14) we find the line of critical points $a_{crit}(s)$ or $\alpha_{crit}(c_s)$ separating the region of continuous transition (small α and/or large c_s) and region of transition with phase co-existence (large α and/or small c_s).

The $a_{crit}(s)$ dependence is presented in Figure 3. As follows from the Figure 3, α_{crit} is virtually constant at small c_s (corresponding to low salt regime) and monotonically increases as a function of c_s at large c_s. The scaling dependence $\alpha_{crit} \sim c_s^{2/3} w^{1/3}$ follows from simple arguments: the transition is continuous if the salt-dominance conditions $\alpha_c c \ll c_s$ are fulfilled in collapsed phase (clearly, if this is the case, then the salt-dominance conditions apply also in the swollen phase). Otherwise, the transition involves the phase co-existence. The density of the collapsed phase at the transition point can be estimated using Eq. (15) and is $c \sim (\alpha/w)^{1/2}$.

Coulomb Interactions Dominated Regime

In the case when Coulomb repulsion dominates over differential osmotic pressure of mobile ions, the equation for the star size can be presented, in analogy to Eq. (13) using the same reduced variables

$$\eta^{8/3} + t\eta - qn^{5/3} = 1 \tag{17}$$

where we have introduced a new parameter

$$q = \frac{c_\theta}{c_q} = \frac{2^{9/8}\pi^{3/4}}{5 \cdot 3^{3/4}} \cdot \alpha^2 l_B N^{3/2} p^{1/4} w^{-3/8}$$

which determines relative strength of the Coulomb repulsive interactions in the PE star; here $c_q \equiv 5(\alpha^2 l_B)^{-1} N^{-2}$ is the monomer unit concentration in the PE star swollen by Coulomb repulsion in the absence of short-range interactions.

As one can easily see from Eq. (17), $\eta(t)$ is a single-valued monotonically decreasing function as long as $q \leq q_{crit} = 4$, while at $q \geq q_{crit}$ the dependence $\eta(t)$ exhibits a van der Waals type loop suggesting discontinuity of the transition between swollen by Coulomb repulsion and collapsed (globular) star conformations. The binodal point, i.e., the value of τ at which the collapsed and the swollen states coexist can be found by equating the corresponding free energies. Alternatively, if we take into account that Coulomb repulsion in the collapsed state is much stronger than that in the swollen state, the transition point can be found from the condition of vanishing of the free energy in the collapsed state:

$$\frac{3}{5} \cdot l_B \frac{(\alpha p N)^2}{R_{collapsed}} - pNw\tau^2 = 0$$

where $R_{collapsed} = (3pN/4\pi\tau)^{1/3}$, that leads to

$$\tau_{tr} \cong (\alpha^2 l_B)^{3/5} (pN)^{2/5} w^{-3/5}$$

The latter expression for the binodal applies also at moderate ionic strength of the solution, that is, in the case of co-existance between swollen conformation which is in the salt dominance regime and collapsed state dominated by Coulomb interactions.

Finally, we remark, that even if the Coulomb repulsion dominates in the swollen state, the collapse of the star may induce "condensation" of the counterions in the globule. This applies if $\alpha(l/a)(p/N)^{2/3}\tau_{tr}^{1/3} \geq 1$.

Conclusions

We have analyzed in a systematic way collapse-to-swelling intra-molecular conformational transition occurring in strongly dissociating star-branched polyelectrolytes upon a decrease in the solvent strength, that is, an increase in the strength of the short-range binary interactions between the monomer units of the star arms. In our analysis we did not make any preassumption concerning localization of the counterions, that is, the dimensions of the minimal electroneutral cell surrounding the star PE macromolecule. On the contrary, the latter was determined independently as a function of the macromolecular architectural parameters (N,p) and the ionic strength of the solution. Our major goal was to analyze the effect of variable ionic strength of the solution on the character (continuous or discontinuous) of the collapse-to-swelling transition and, in the case of discontinuous transition, on the localization of the transition point (the value of the solvent strength corresponding to co-existence of swollen and collapsed conformations).

In full agreement with our earlier findings [15] we have demonstrated that collapse-to-swelling transition in salt-free solution of PE stars, whose swelling is determined by osmotic pressure of confined counterions, features the first order phase transition, i.e., involves co-existence of collapsed and swollen states. An increase in the bulk concentration of added salt leads to decrease of the differential osmotic pressure, to a progressive shift of the transition point toward less poor solvent strength conditions and to a decrease in the difference in the monomer unit densities in co-existing at the transition point collapsed and swollen conformations. Finally, at sufficiently high salt concentration the collapse-to-swelling transition recovers progressive character, similar to that of the corresponding transition in neutral star-like macromolecules. We have derived a critical value of the added salt concentration corresponding to the vanishing of the difference in densities of co-existing phases, as a function of the degree of ionization, number of arms and their degree of polymerization. In particular, we have shown that the critical salt concentration increases as $\sim \alpha^{3/2}$ with increasing ionization of the star arms.

We have also demonstrated similar trends for the collapse-to-swelling transition in PE stars with small number of arms, where at low ionic strength the Coulomb repulsion of arms provides the leading contribution to the overall force inducing the arms stretching.

Finally, we have to emphasize, that exploited here box-like model (equivalent to the classical Flory approach) enables us to capture properly such essential feature of the conformational transition as occurance of the (micro)phase coexistence and to localize the transition point. However, unraveling of the details of evolution of the intra-molecular structure in the course of the collapse-to-swelling transition requires more elaborated analysis, that will be presented in future publication.

[1] E. B. Zhulina, O. V. Borisov, T. M. Birshtein, *Polym. Sci. USSR* **1988**, *30*, 774.

[2] K. Karaky, S. Reynaud, L. Billon, J. Francois, Y. Chreim, *J. Polym. Sci. Part A, Polym. Chem.* **2005**, *43*, 5186.

[3] F. A. Plamper, H. Becker, M. Lanzendörfer, M. Patel, A. Wittemann, M. Ballauff, A. H. E. Müller, *Macromol. Chem. Phys.* **2005**, *206*, 1813.

[4] F. A. Plamper, M. Ruppel, A. Schmalz, O. V. Borisov, M. Ballauff, A. H. E. Müller, *Macromolecules* **2007**, *40*, 8361.

[5] F. A. Plamper, A. Walther, A. H. E. Müller, M. Ballauff, *Nano Lett.* **2007**, *7*, 167.

[6] D. V. Pergushov, I. A. Babin, F. A. Plamper, A. B. Zezin, A. H. E. Müller, *Langmuir* **2008**, *24*, 6414.

[7] P. Pincus, *Macromolecules* **1991**, *24*, 2912.

[8] O. V. Borisov, *J. Phys. II (France)* **1996**, *6*, 1.

[9] O. V. Borisov, E. B. Zhulina, *Europ. Phys. J. B*, **1998**, *4*, 205.

[10] J. Klein Wolterink, F. A. M. Leermakers, G. J. Fleer, L. K. Koopal, E. B. Zhulina, O. V. Borisov, *Macromolecules* **1999**, *32*, 2365.

[11] F. A. M. Leermakers, M. Ballauff, O. V. Borisov, *Langmuir*, **2008**, *24*, 10026.

[12] M. Roger, P. Guenoun, F. Muller, L. Belloni, M. Delsanti, *Eur Phys. Journ. E* **2002**, *9*, 313.

[13] A. Jusufi, C. N. Likos, M. Ballauff, *Colloid Polym. Sci.* **2004**, *282*, 910.

[14] Y. Mei, M. Hoffmann, M. Ballauff, A. Jusufi, *Phys. Rev. E* **2008**, *77*, 031805.

[15] O. V. Borisov, T. M. Birshtein, E. B. Zhulina, *Progr. Coll. Polym. Sci.* **1992**, *90*, 177.

[16] R. Ross, P. Pincus, *Macromolecules* **1992**, *25*, 2177.

[17] S. Misra, W. L. Mattice, D. H. Napper, *Macromolecules* **1994**, *27*, 7090.