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Microphase Coexistence in Polymeric Brushes

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Summary: A collapse of polymeric brushes in a solvent can be induced by a change in external conditions, for example, solvent quality or its temperature. The systems with following specific interactions are considered in this paper, namely, polyelectrolyte brushes, amphiphilic brushes in a mixture of incompatible solvents, and brushes with possibility of liquid-crystalline ordering of polymer segments. For all the systems it is shown that the brush collapse can be observed under certain conditions, and it occurs through a microphase segregation. There are two microphases of different densities that coexist in the brush. The effect is caused by general properties of the swollen phase of polymeric brush and hence appears at all types of the interactions that can induce a phase transition of the brush into collapsed state.

Keywords: brush, collapse, liquid crystalline polymers (LCP), phase separation, polyelectrolytes

Introduction

In this paper we consider the polymer systems with a possibility of the phase transition, which can occur under certain conditions, though the volume of a new phase at a point of the phase transition is very small. This situation is observed, for instance, while polymers crystallize, though, contrary to the degree of polymer crystallinity, in our systems this new phase grows up to its limiting value following the change of external conditions.

The paper is based on a series of investigations carried out during a number of years. Besides the authors, Ekaterina Zhulina, Oleg Borisov, and Victor Pryamitsyn participated actively in these investigations as well as our friends and colleagues from the University of Wageningen (the Netherlands), namely, G. Fleer, F. Leermakers, and their collaborators[1-6].

Polymeric brush is an object of our theoretical investigation based on numerical analysis of the self-consistent-field (SCF) equations carried out in the approximations elaborated by Scheutjens and Fleer[7]. All calculations are done using either an original program at the University of Wageningen or a program developed in the same formalism at the IMC in St.Petersburg.

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We will not describe the method of calculations in much detail just mentioning that we assume the polymer brush to be homogeneous in a lateral direction and consider a lattice model of polymer chains in the brush in its traditional formalism proposed by Flory.

Scenario of Phase Transition at Brush Collapse.

Here we consider collapse of the brush immersed in a solvent, which occurs as a phase transition. To accomplish this, certain of the specific interactions should be present in the brush: interactions between mesogenic groups incorporated into the grafted polymer chains that can result in the LC order of the collapsed phase[1,3,5]; in polyelectrolyte brushes the entropy contribution to the free energy of neutralizing counter ions [2,3]; a tendency to n – cluster organisation introduced into discussion for polymer systems by de Gennes and particularly for brushes by Brochard et al.[8,9]; amphiphility of the polymer in a binary solvent with limited component compatibility[4,6]. In all these cases the brush collapses by the phase transition at least if the grafting density is not too high. The scenario of the collapse is the same in all the cases, though governing parameters that should be changed to initiate the collapse are different.

The key feature of this scenario is that the brush collapse occurs through a microphase segregation: two microphases of different densities coexist in the brush.

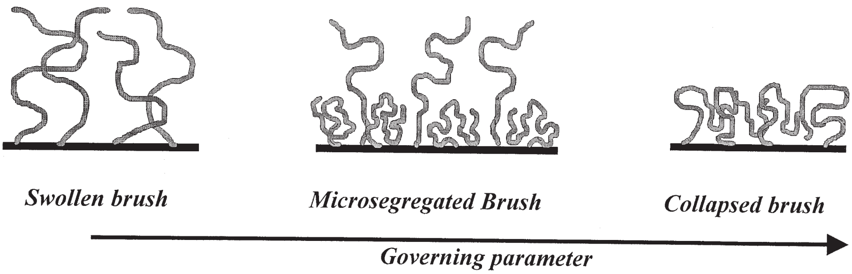


Figure 1. Schematic representation of the phase separation inside the brush. At the phase transition point the collapsed phase appears at the interior of the brush. This phase coexists with the swollen outer part. The portion of a collapsed polymer grows together with the governing parameter

We now represent some theoretical results, which form a basis for this schematic picture.

The density profiles $\rho(x)$ (a) and the free ends distribution $g(x)$ (b) for a polyelectrolyte brush in a salted water solutioon are represented on the fig.2. The ionic strength of the solution is 10^{-5}M; polymer chains length, N=500; surface grafting density, σ = 10^{-2}, the ionization degree: α=0.2 [3.5]. In a good solvent at $\chi = 0$ (χ - the Flory – Huggins parameter), the brush is swollen, at $\chi = 2.5$ the solvent precipitates the brush, so it is completely collapsed, at $\chi = 1.9$ the coexistence of the two phases is clearly seen.

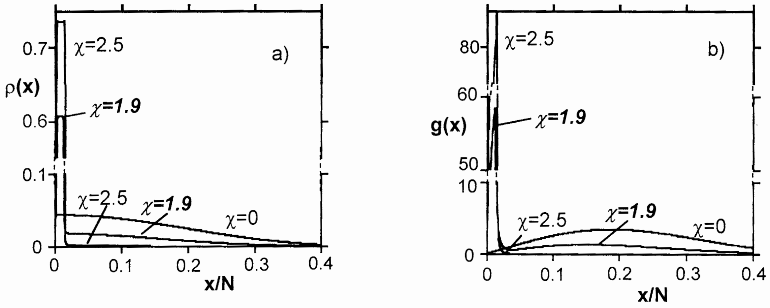


Figure 2. The collapse of a polyelectrolyte brush.

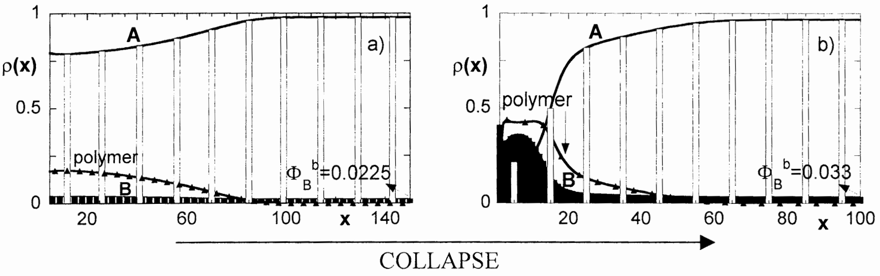
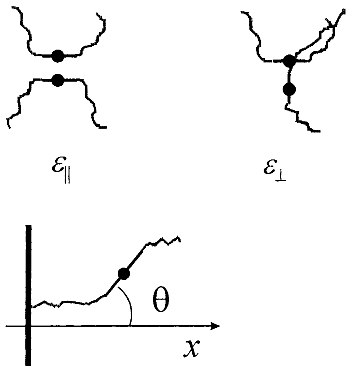


Figure 3. The collapse of an amphiphilic brush: polymer density profiles and the profiles of the solvents A and B concentrations at two values of the amount Φ_B^b of admixture B added to the bulk.. Φ_B^b=0.0225 (a) and 0.033 (b). The other parameters are: N=100, σ=0.02, $\chi_{AB} = 3.5$, $\chi_{PA} = 0.3$, $\chi_{PB} = 0$

The similar phase coexistence can be seen on fig.3. In this case the collapse of an amphiphilic brush with the change of binary solvent composition takes place. The solvent consists of two components with limited compatibility (for further information see [4,6]). It is interesting that the polymer chains absorb the better solvent at an extremely small amount of this admixture in the bulk, and then suddenly collapse to a very dense sub layer.

The other most extensively studied system is a polymer brush that undergoes a thermotropic LC transition in a solvent. This transition occurs as the flexible polymer chains contain mesogenic segments with anisotropic interactions between them described by parameter η. The ordering of the brush is characterized by order parameter S_2 with respect to the director of the nematic ordering ***x*****,** turned perpendicularly to the grafting plane (fig.4).



$$\eta = -\frac{\varepsilon_{\|} - \varepsilon_{\perp}}{kT}$$

$$S_2 = \frac{\overline{3\cos^2\theta - 1}}{2}$$

Figure 4. Parallel and perpendicular segment - segment interactions as well as the definition of η-value and the order parameter.

If ρ is the segment density, χ is the Flory-Huggins interaction parameter, and contribution of anisotropic interactions is taken into account in Maier-Saupe approximation, then the free energy in each x layer is given by the following relation:

$$F_{int}(\rho) = (1-\rho)\ln(1-\rho) - \chi\rho^2 - \frac{1}{2}\eta\rho^2 S_2^2,$$

where ρ and S_2 are functions of x.

The evolution of this system characteristics with the change in the governing parameter η is represented on the fig.5. The transition to the microphase segregated state and the gradual increase of the LC microphase is observed with increase in η.

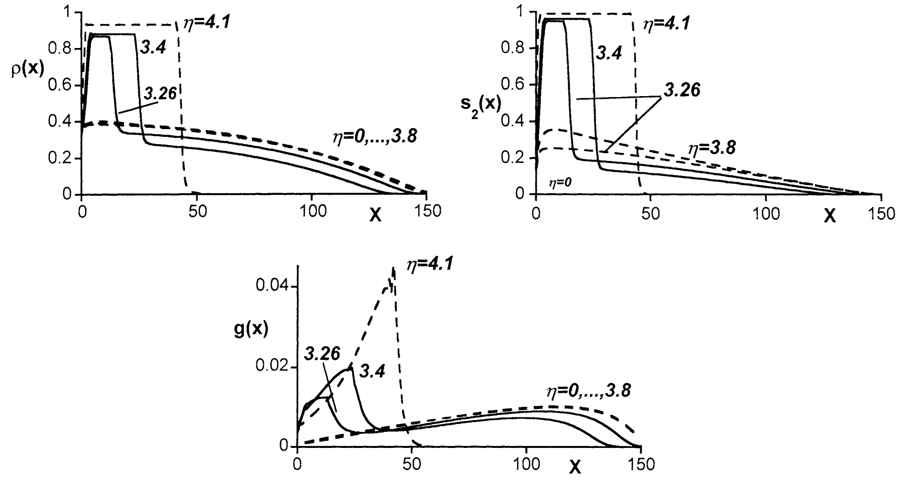


Figure 5. The evolution of the brush characteristics with increase in η. N=500; σ=0.1.

The Peculiarity of the Phase Transition in Brushes.

At the transition point, the thickness of the LC microphase scales as $N^{1/2}$ in contrast to overall thickness proportional to N (fig.6). Hence, the fraction of segments in initial LC phase scales as $N^{-1/2}$ and the greater is N the less is the jump of brush properties at phase transition point. At $N\rightarrow\infty$ the transition is virtually continuous[1,3]. The position of transition point tends to smaller values of η upon increase in N.

The other peculiarity of the transition is that the chains are separated into two groups, namely, **intrinsic chains** that are completely in the collapsed phase and **transit chains**, which pass through the collapsed microphase to the swollen layer. The evidence for that is the form of free end distribution curves ***g(x)*** with two well defined maximums (fig.6).

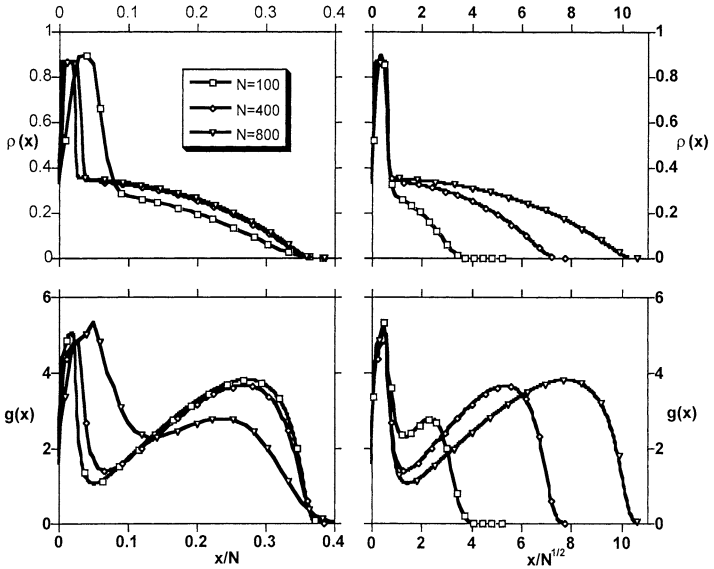


Figure 6. The scale of the LC microphase in the transition point

Existence of the collapsed phase does not affect significantly the density and the degree of extension S_1 for transit chains. Meanwhile these chains as inner chains have a high degree of order in the LC microphase (fig.7).

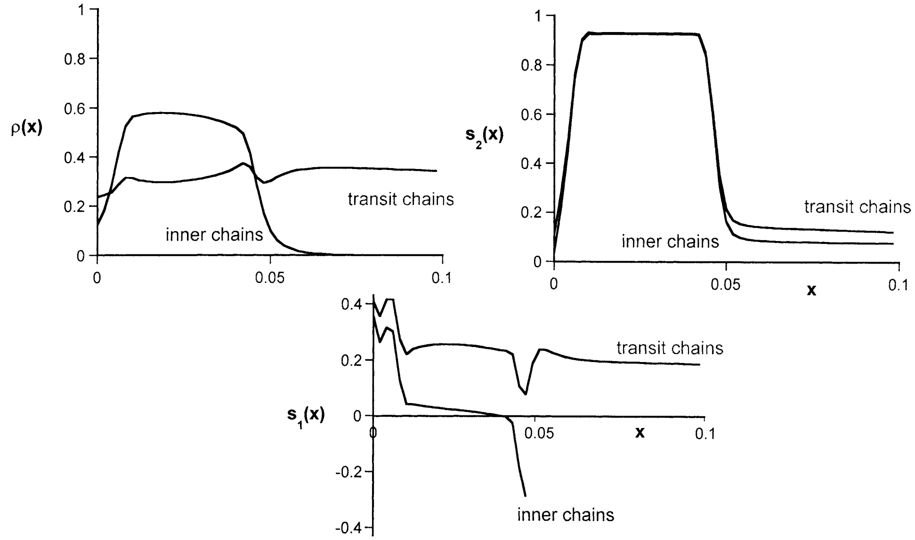


Figure 7. Partial characteristics of inner and transit chains

Why does the Phase Transition Occur Through the Microphase Segregation with Formation of Group of Inner Chains?

It is because of the tendency of chains to go out from the swollen phase. This is related to the form of the the free energy of the swollen brush, which is proportional to N but scales as $\sigma^{5/3}$ (here σ is the grafting density):

$$F = AN\cdot\sigma^{5/3}$$

Hence the free energy of the swollen brush after removing the fraction ε **of chains** (fig.8b):

$$F^{(chains)} = F_0(1-\varepsilon)^{5/3} \cong F_0\left(1-\tfrac{5}{3}\varepsilon + O(\varepsilon)\right)$$

Is below the free energy of the swollen brush after removing the fraction ε **of segments in each chain** (fig.8a): $F^{(seg)} = F_0(1-\varepsilon)$

$$F^{(chains)}(\varepsilon) < F^{(seg)}(\varepsilon)$$

From the two possible paths of partial ordering the brush selects the most favorable (fig.8b)

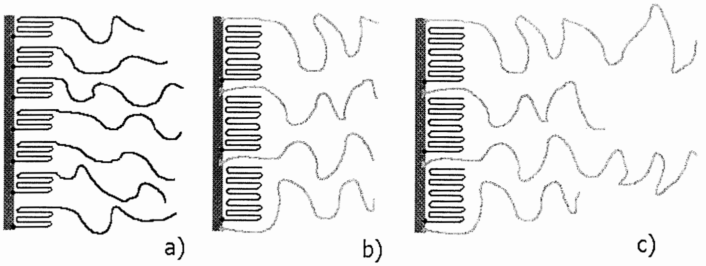


Figure 8. Two paths for partial collapse in a brush: collapse of fractions of all chains (a), collapse of fraction of chains (b). Case b with the lengthening of a part of transit chains (c)

Mixture of Short and Long Chains.

As follows from fig.8b, the lengthening of transit chains (or part of transit chains) should not affect the position of the transition point (fig.8c). This transition involves only short chain, provided the fraction of short chain is sufficient to form the collapsed microphase (fig.9), i.e.:

$$\varepsilon_{long}^{(mixture)} < (1-\varepsilon_t)\cdot$$

At the transition point only few chains collapse, so the lengthening of a major part of all chains does not affect the transition conditions significantly (for instance, at σ=0.1, the transition does not "feel" the lengthening of up to 80% of the short chains with initial length N_2=200).

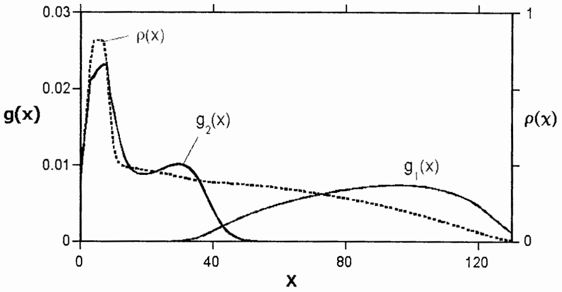


Figure 9. Distribution of density and free chain ends for bidisperse brush

Further increase of the governing parameter leads to an increase of the collapsed microphase. At a significant difference in chains length, the short chains totally collapse at lower η values than one need for long chains just to start the collapse. In this case the collapse of a brush has two stages (fig.10). The short chains collapse at a 1st order phase transition mechanism (the characteristics jump decreases with increase in chain length). The long chains collapse at a 2nd order phase transition mechanism, similar to the collapse in a monodisperse brush at $N \rightarrow \propto$ limit. The position of this phase transition is determined by the grafting density σ_1 of longer chains only.

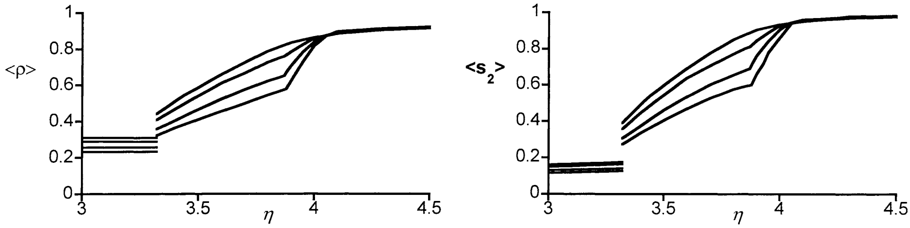


Figure 10. Two step ordering in bidisperse brushes, $N_2 = 200$; $\sigma_1 = 0.01$; $\sigma_2 = 0.09$, N_1 from top to bottom: .200; 400; 800; 1200

Conclusions

Polymer brush is a good example of nonhomogeneous loosely bound self-organizing polymer system with a wide range of conditions under which microphase segregation occurs.

The nature of the effect lays in structural reorganization and in increasing stability of the initial (high temperature) phase as low temperature phase develops.

This effect is related to the transition of whole chains from the swollen to the collapsed phase (all-or-none transition for individual chains).

The effect is caused by general properties of the swollen polymer brush and hence appears at all types of the interactions in brushes that can induce a phase transition into collapsed state.

Position of the transition point is not affected by lengthening of up to 80% of the short chains (initial length N_2=200)

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