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Theory of Liquid-crystalline Ordering in Polymer Brushes

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Summary: We present a review of the works devoted to investigation of LC ordering in polymer brushes. This series has been carried out by the group of T. M. Birshtein and covers the following aspects of the problem: thermotropic LC phase transition in LCP brushes, microphase segregation, homeotropic and planar LC phases, LC polymer in LC solvent, lyotropic LCP brushes, LC transitions under normal or lateral force (shear flow). Analytical theory is developed for simplified model of polymer brush with accounting for thermotropic attraction in Mayer-Saupe approximation and lyotropic repulsion in DiMarzio formalism; numerical calculations are fulfilled in self-consistent field approximation (method of Scheutjens and Fleer). Brownian dynamics simulations are applied for modeling polymer brush in a shear flow.

Keywords: liquid-crystalline polymers (LCP); modeling; monolayers; phase diagrams; phase separation; self-organization; shear; simulations; theory

Introduction

Grafted polymer layers or polymer brushes are well-known as superstructures aimed for modifying surface properties and, hence, interactions of the surface with its medium. Functional polymer brushes, i.e. brushes of polymer chains with special functional groups, are in the focus of both theoretical and experimental investigations.[1] Liquid-crystalline polymer (LCP) brushes are of special interest since they can be used for preparing alignment layers for liquid-crystalline displays (LCD). This idea has been formulated by A. Halperin and D. R. M. Williams in 1993[2,3] and has inspired a series of theoretical studies in this field.[4–10] However a progress in synthesis and experimental investigations of LCP brushes has been achieved just recently. Thermotropic LCP brushes are synthesized and investigated in Mainz[11] and in Cambridge (UK),[12] and lyotropic LCP brushes are prepared and studied in St.Petersburg.[13] This significant progress in experimental approaches to the problem encourages giving a special review of theoretical investigations of LCP brushes that have been carried out in the group T. M. Birshtein for almost ten years.[14–30]

The following aspects of the problem are considered. Investigation of thermotropic LC transition in polymer brush includes studies of the brushes with mesogenic fragments in main chains and in side chains in non-mesogenic solvent (thermotropic LC phase transition, microphase segregation, homeotropic and planar LC phases), main chain LC polymer in LC solvent, lyotropic main chain LCP brushes, LC transitions under normal or lateral force (shear flow). Analytical theory is written for the lattice box-model in approximation of Alexander and de Gennes.[31,32] For numerical calculations, self-consistent field approximation in formalism proposed by Scheutjens and Fleer[33,34] is applied. All interactions between polymer and solvent molecules are considered in the framework of Flory-Huggins mean-field theory.[35] Mutual interactions between mesogenic fragments in thermotropic LC are accounted by Mayer-Saupe mean-field theory. For

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lyotropic LCP, modification of DiMarzio lattice model[36] is applied. Grafting density of the chains σ and number of segments in the chain N are specific parameters of the system.

Thermotropic LC Transition in Polymer Brush

Thermotropic liquid crystals are specified by anisotropic interactions between mesogenic fragments. This means that polarization is different for parallel and normal mutual orientation of the fragments, Figure 1. The interaction parameter η is defined by the difference of corresponding energies related to the temperature.

In the case under consideration mesogenic segments are incorporated into polymer chains, the chains itself are supposed to be flexible. In the mean field approximation the free energy density F_{int} of the system is

$$F_{\text{int}} = (1-\Phi)\ln(1-\Phi) - \chi\Phi^2 - \frac{1}{2}\eta\Phi^2 S_2^2 \quad (1)$$

Here Φ is the segment density and the first term in Equation (1) gives conformational entropy; χ is the Flory-Huggins parameter describing polymer-solvent interactions. The last term in Equation (1) describes anisotropic interactions in the system in Mayer-Saupe self-consistent field approximation, where S_2 is the order parameter defined through an averaged value of orientation of the segment with respect to the director of LC phase (Figure 2):

$$S_2 = \frac{3\langle\cos 2\Theta\rangle - 1}{2} \quad (2)$$

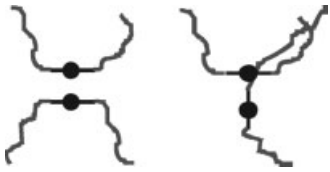

Figure 1.
Parallel and normal mutual orientation of the mesogenic fragments.

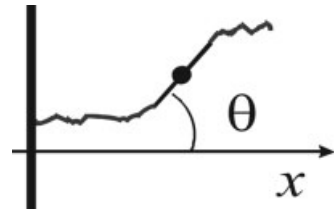

Figure 2.
Orientation of the chain segment with respect to LC director.

Polymer chains tend to stretch in normal direction to the grafting surface and thus we can suppose that director x of LC orientation for LCP brushes with mesogenic fragments in main chains is induced in this direction.

Analytical theory of LC ordering of polymer brushes has been written for the box (or accordion) lattice model proposed by Alexander and de Gennes.[31,32] This simple model allows obtaining rather clear results though certainly it has evident restrictions due to suggestion of fixing the chain ends at the same height of the brush. Equilibrium states of the system are determined by the free energy minimization with respect to the order parameter S_2. For the box model, equilibrium value of S_2 is universal for the brush. The director of LC phase is assumed to be normal to the grafting surface for the main chain LCP and parallel for the side chain LCP brushes. For LCP brushes with mesogenic fragments in side chains, the lattice model with one preferred orientation for the segments parallel to the grafting surface and, hence, normal to the direction of stretching is applied. In Figure 3a–b we summarize our results for LCP brushes with mesogenic fragments in main chains and in side chains (see ref.[14,16,23] for details).

Phase diagram in (η, Φ) –coordinates is given in Figure 3a, it collects binodal points for the brush under grafting density variation. It is seen that thermodynamic behavior of LCP brushes with mesogenic segments in main chains and in side chains is similar and specified by the following features. Transition from isotropic to anisotropic phase occurs as a first order

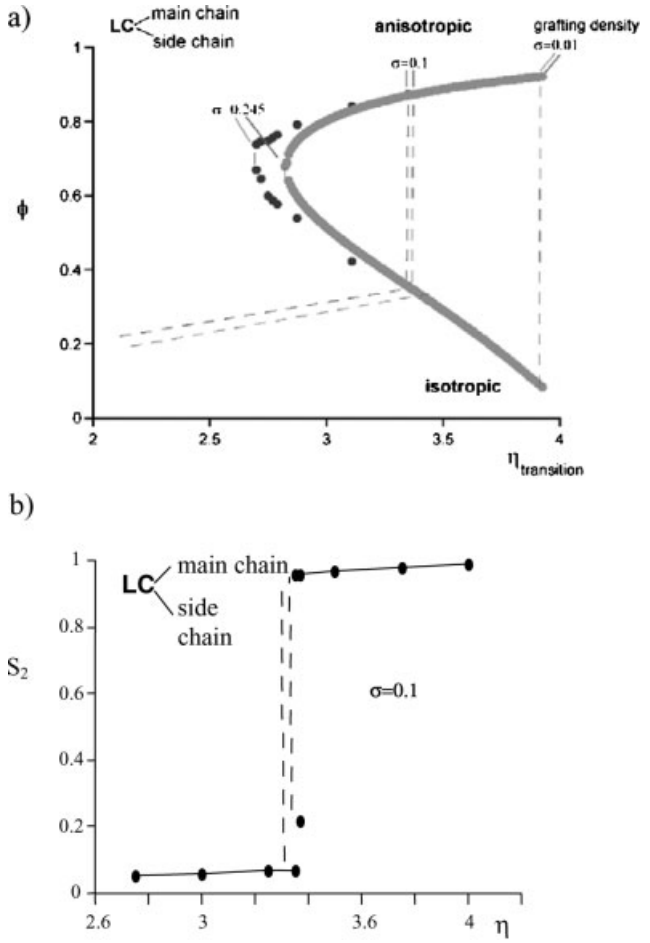

Figure 3.
Polymer density of isotropic and anisotropic phases at the energy of phase transition $\eta_{transition}$ (a) and order parameter S_2 of the nematic phase as a function of η (b, grafting density $\sigma = 0.1$) for polymer brushes with mesogenic segments in the main chains (solid lines) and in the side chains (circles).

phase transition with a jump in polymer density for a wide range of values of the grafting density σ. Phase diagram has a critical point: in the case of very sparse grafting anisotropic phase occurs continuously (critical behavior of the system is discussed in ref.[19]). Noteworthy, polymer density in anisotropic phase is very high and thus the phase is very compact or almost collapsed. Since it is well-known that stretching of chains is typical of LC polymers in anisotropic phase, this result is rather unusual and is a consequence of restriction in polymer mobility caused by the grafting.

In Figure 3b the order parameter S_2 is shown as a function of η for the brush with the value of grafting density $\sigma = 0.1$. The values of S_2 in anisotropic phase are close to unity and hence LC phase is highly ordered even at the point of phase transition.

Numerical calculations carried out for LCP brush in self-consistent field approximation (method of Scheutjens and Fleer[33,34]) supply us with important information about the brush structure in isotropic and anisotropic phases, ref.[15]. In Figure 4a–c we collect data for polymer density profiles, free ends distributions, and distributions of the order parameter. In

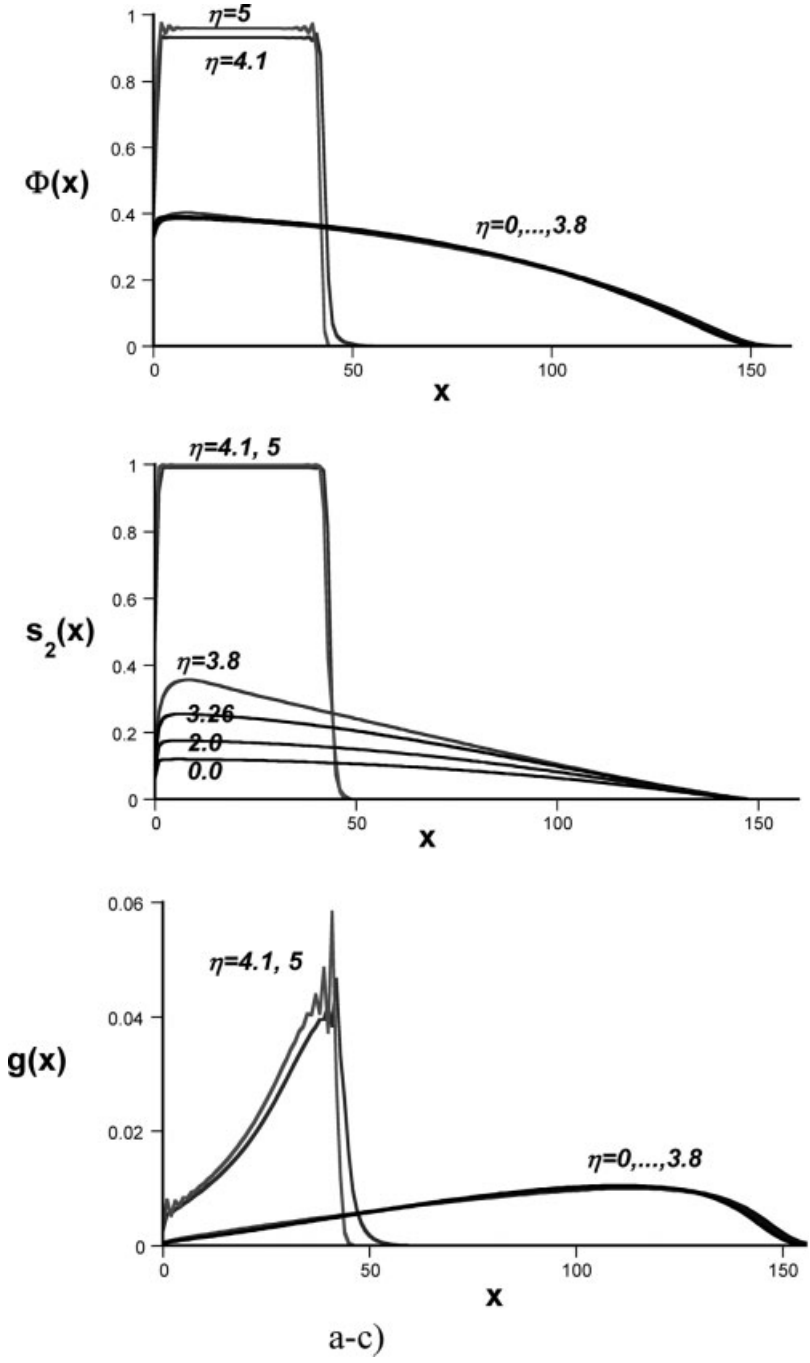

Figure 4.
Distribution of segment density (a), order parameter (b) and free ends (c) for LCP brush with mesogenic segments in main chains (grafting density $\sigma = 0.1$). At $\eta = 0$ 3.8 the brush is swollen in isotropic phase, at $\eta > 4$ it is collapsed in LC state.

isotropic phase polymer brushes are specified by parabolic-like polymer density profiles typical of the brush swollen in a good solvent while in LC phase polymer density is so high that it allows concluding of the brush collapse (Figure 4a). The free ends distribution (Figure 4b) in isotropic phase has a typical of swollen brush shape, whereas in anisotropic phase it is sharp and also signals collapse. Anisotropic phase is well-ordered from the beginning of its formation: the order parameters in Figure 4c get values close to unity at the point of phase transition.

Microphase Segregation in LCP Brush

Polymer brush can collapse under changing of external conditions, namely, changing of solvent affinity, temperature etc. The results summarized in the previous section show that phase transition from isotropic to anisotropic state in LCP brush also occurs as a collapse. It is of much importance to understand how this transition rises. For this reason pre-transition brush behavior has been studied in details.[19,22,23] Figure 5a–c present results of corresponding numerical calculations, which evidently show that phase transition occurs through microphase segregation of the brush. In Figure 5a one observes a range of η values, where two microphases specified by low and high densities coexist in the brush. Free ends distribution also demonstrates coexistence of two microphases, Figure 5c. At a certain value of η, dense LC microphase appears in the swollen isotropic brush and increases in volume with following increase in η. LC nature of the dense phase is well confirmed by high values of the order parameter (Figure 5b).

The process is sketched in Figure 6: it is a phase transition with extended microphase coexistence.

Formation of Homeotropic and Planar LC Structure

LCP brush in anisotropic phase forms a rather dense layer with high orientation. The next question is whether this structure is homeotropic (with orientation normal to the grafting surface) or planar (with orientation parallel to the grafting surface). Homeotropic structure (HLC) is specified with the value of the order parameter $S_2 = 1$ for total ordering while the limiting value of S_2 in planar structure (PLC) is $S_2 = -0.5$, Figure 7.

A series of numerical calculations[20,30] has been carried out for clarifying the problem and the results make possible the following conclusion: homeotropic LC structure is always of the lower free energy, planar structure is metastable. The free energy F and the order parameters S_2 are given in Figure 8 and 9 as functions of interaction parameter η for low (Figure 8) and high (Figure 9) values of grafting densities.

At high grafting density, homeotropic LC structure is favorable. At low grafting density, numerical procedure leads either to planar or to homeotropic LC structure. Concerning real LCP brushes, surface affinity can induce ordering of the planar LC structure at low grafting density. We do not know corresponding experiments but Monte Carlo simulations of LCP brushes carried out by H. Lange and F. Schmid[4] give the same result though it should be noted that the chain length in this simulations has been too short (4 segments) to describe polymer system properly.

LC Polymer in LC Solvent

Recently investigation of thermotropic LC polymer immersed into a nematic solvent has been started. Here we present some results. A capability of the polymer for LC ordering is much weaker than that of the solvent. For comparison the opposite case of a strong nematic polymer and weak nematic solvent is discussed.

In the case of nematic solvent contribution of anisotropic interactions to the free energy is more complicated due to the ordering not only of the polymer segments but of the solvent molecules as well. There are three different parameters of thermotropic interactions: solvent-solvent η_{ss}, polymer-polymer η_{pp}, and solvent-polymer (or polymer-solvent) η_{sp}. Hence contribution

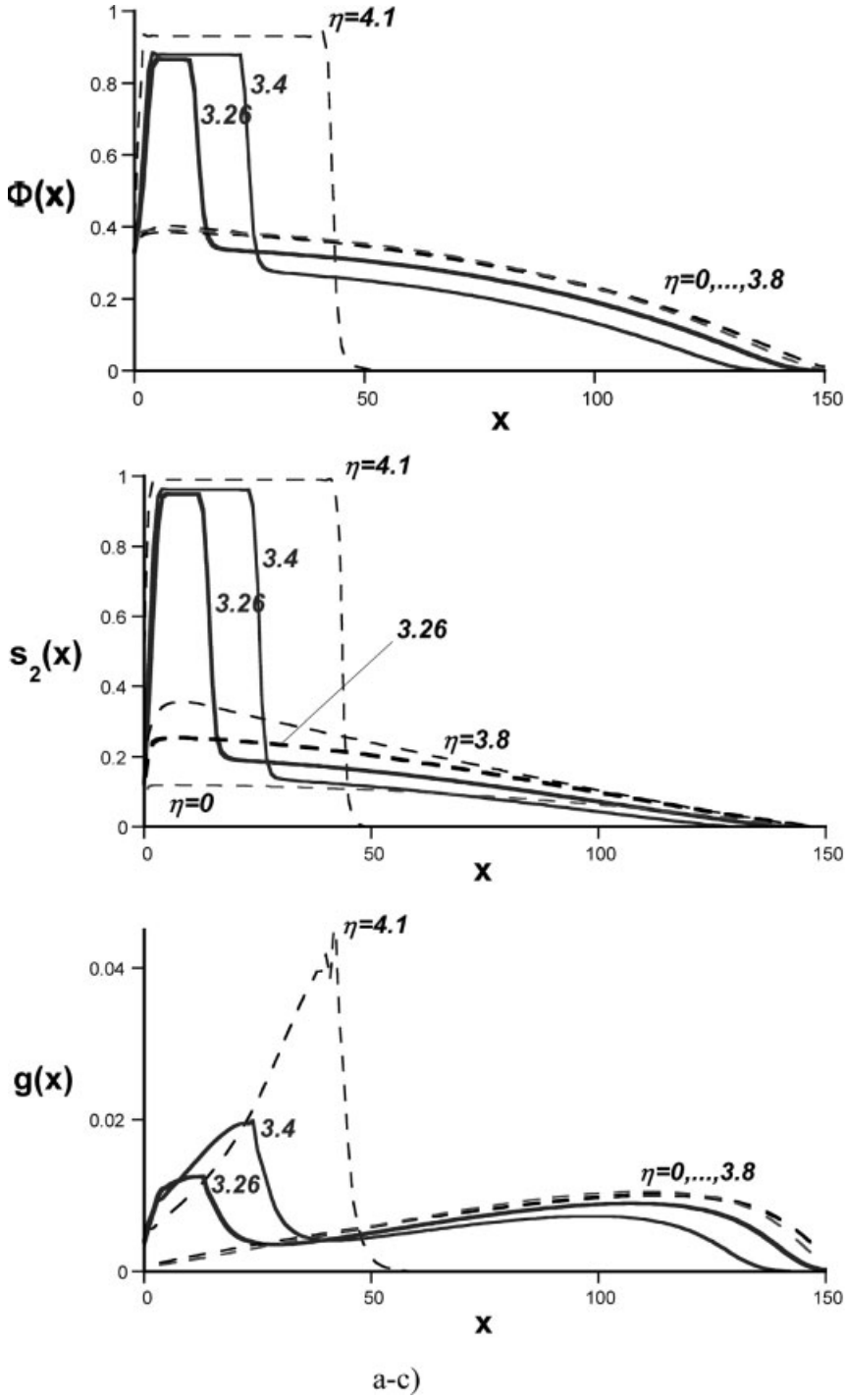

Figure 5.
Distribution of segment density (a), order parameter (b) and free ends (c) for microsegregated LCP brush with mesogenic segments in main chains (grafting density $\sigma = 0.1$). Microsegregated brush (MSB) contains two microphases. The volume of dense LC microphase increases with an increase in η.

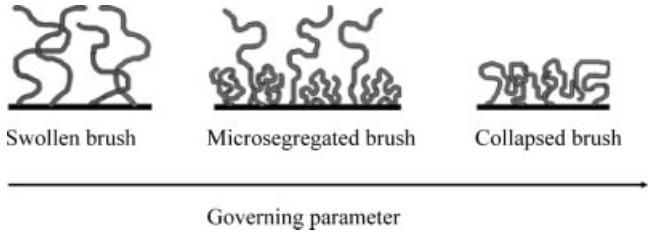

Figure 6.
Brush collapse through microphase segregation.

of anisotropic interactions to the free energy density given by the last term in Equation (1) for LCP brush in non-mesogenic solvent now appears to get the following form:

$$F_{anis} = -\frac{\eta_{ss}}{2}(1-\Phi)S_s^2 - \eta_{sp}\Phi(1-\Phi)S_sS_p - \frac{\eta_{pp}}{2}\Phi^2 S_p^2 \quad (3)$$

Here S_s, S_p give order parameters of solvent and polymer segments, respectively. An assumption of intermediate type of anisotropic interations between polymer and solvent molecules is introduced in the form $\eta_{sp} = \sqrt{\eta_{ss} \cdot \eta_{pp}}$ and thus only two interaction parameters remain in Equation (3). Conformational entropy of solvent molecules and polymer segments

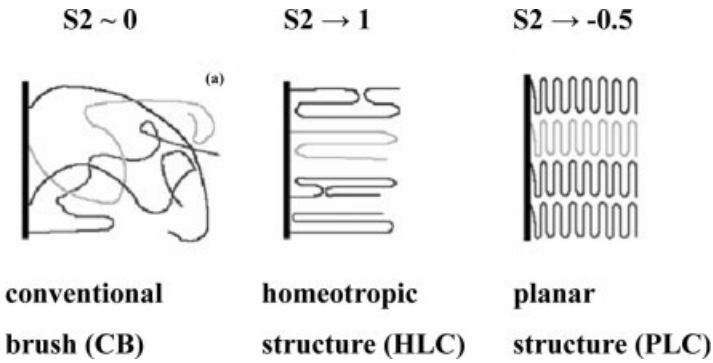

Figure 7.
Swollen conventional brush in isotropic phase in two possible LC phases for LCP brush, homeotropic and planar.

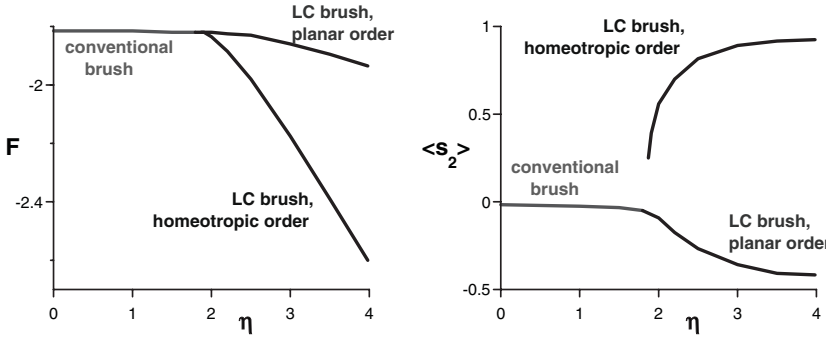

Figure 8.
Free energy F and order parameter S_2 for LCP brush at low grafting density (grafting density $\sigma = 0.04$) as functions of η.

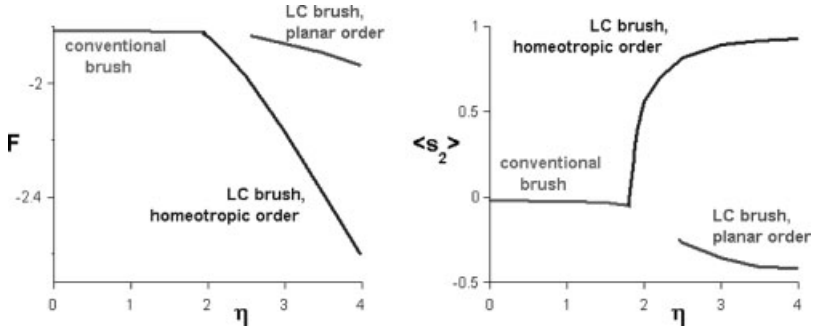

Figure 9.
Free energy F and order parameter S_2 for LCP brush at high grafting density (grafting density $\sigma = 0.1$) as functions of η.

and translational entropy are accounted for in traditional way. The procedure of the phase diagram constructing is similar to that described for LCP brush in non-mesogenic solvent though more complicated due to necessary minimization of the free energy with respect to the both order parameters S_s, S_p.

Figure 10 shows phase diagram of nematic polymer in nematic solvent in coordinates (inverse temperature T_0 /T – polymer density φ_p, where $T_0 \approx 1.85 T_p(\mathrm{tr})$). Left part corresponds to the case when inverse temperature of the LC transition for polymer is twice higher than for solvent whereas in the right part it is twice lower. Anisotropic and isotropic phases are denoted as N and I in Figure 10.

Right-hand part of the phase diagram in Figure 10 is of prominent interest. It is seen how polymer under decreasing temperature forms dense LC phase and with following decrease of the temperature involves more and more solvent inducing its LC ordering at higher temperature than temperature of the solvent phase transition. This effect is remarkable in the context of possibility to induce alignment near surfaces modified by LCP brushes, the problem being of main importance in producing LC devices. It should be mentioned that in experimental work carried out by Bin Peng and Rühe[11] LCP brushes have been synthesized and their solutions in nematic solvents studied. The phase diagram shows a rather similar effect to that in

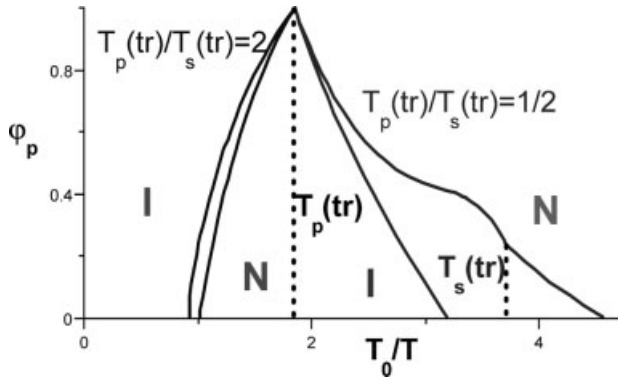

Figure 10.
Phase diagrams of nematic polymer in nematic solvent in coordinates (inverse temperature T_0 /T – polymer density φ_p).

Figure 10 for LC polymer in nematic solvent.

Lyotropic LCP Brushes

Lyotropic LC phase occurs due to repulsion of fragments with geometrical asymmetry of the form and is effected not by the temperature but the concentration of the solution. Asymmetry is defined as relation of long and short axis of the fragment and is a governing parameter for lyotropic LCs. We use a modified Di Marzio lattice model[36] to construct the free energy density for the brush of free joint rod-like fragments:

$$F = -\frac{1}{N}\ln G - \ln \Phi + p\chi(1-\Phi) \qquad (4)$$

Here G is a number of ways to place N rod-like molecules of length p in the simple cubic lattice. The second term excludes translational entropy of the segments due to their grafting (brush effect). Polymer-solvent interactions are described by Flory-Huggins parameter χ and involved by the last term in Equation (3). All the details are given in ref.[28] while here we would like to show only some of the results. In Figure 11 the phase diagram in (Φ, χ) variables for lyotropic LCP brush is presented ($p = 7$), corresponding phase diagrams for rods and free joint polymer of rod-like segments are given for comparison. In contrast to polymer solution, anisotropic phase occurs in the brush as the first order phase transition only at $\chi > \chi^*$.

Transitions in LCP Brushes Under Shear Flow

Finally we would like to summarize some of the results concerning LCP brush under deformation. This kind of investigations has been started from normal deformation of LCP brush studied in the framework of Alexander and de Gennes model.[17] Investigation of LCP brush in shear flow has been

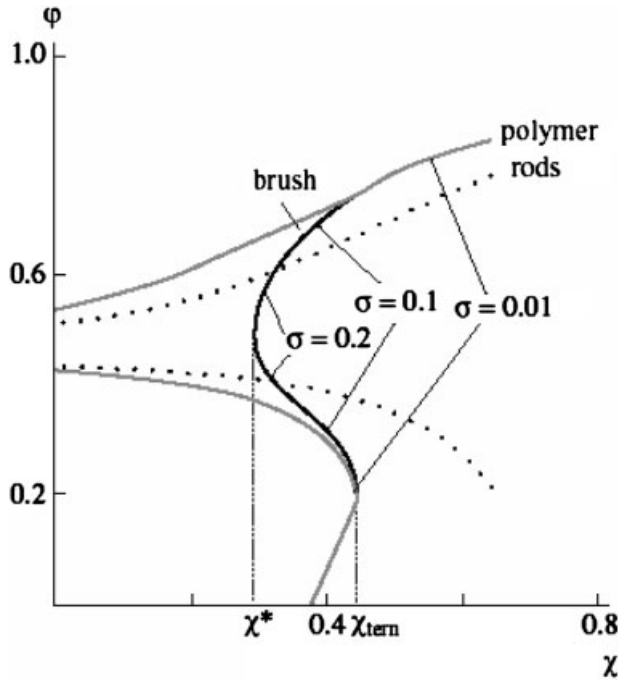

Figure 11.
Polymer density of isotropic and anisotropic phases at the point of phase transition $\chi_{transition}$ for lyotropic LCP brushes of various values of the grafting density σ and for solutions of rods and polymers combined of free joint rod-like fragments.

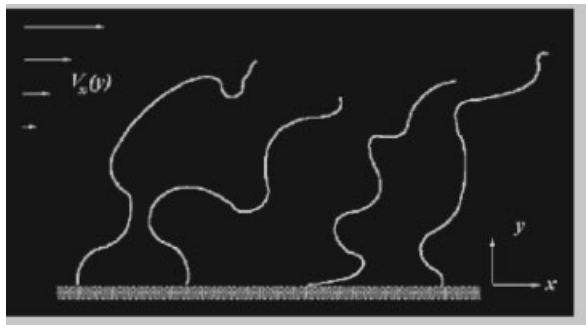

Figure 12.
Polymer brush under an influence of lateral force.

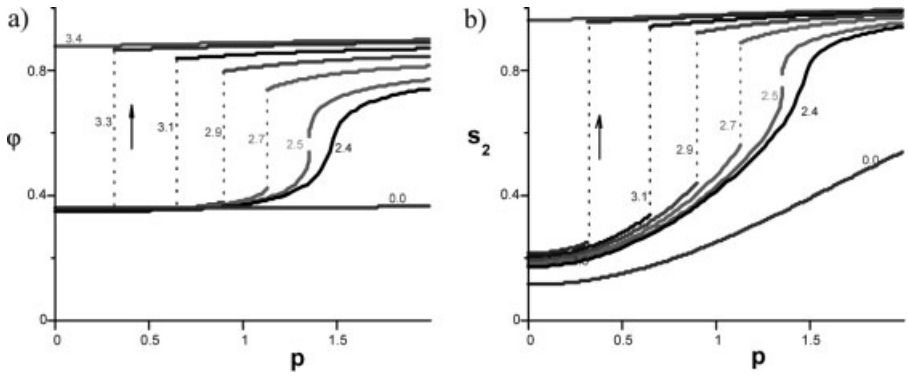

Figure 13.
Polymer density φ (a) and order parameter S_2 (b) of LCP brush given as functions of the force p of applied shear flow.

carried combining a self-consistent field approach and Brownian dynamics simulation.[25–27] The model is shown schematically in Figure 12.

It has been shown that lateral force can induce the compression of LCP brush at shear rates much smaller than those which induce the compression of isotropic brush. As normal deformation, lateral flow can induce LC phase transition that occurs as brush collapsing. At large shear rates, chain distribution appears to be bimodal: one fraction of the chains is highly stretched while another is unperturbed by the flow.

Figure 13 presents the averaged values of polymer density (Figure 13a) and order parameter (Figure 13b) of LCP brush as functions of the applied force (see ref.[27] for the details). At $p > 2$ the flow induces the LCP brush collapse, the brush itself being in pre-transitional LC state, Figure 13a. LC phase induced by the shear flow is specified by high values of the order parameter, Figure 13b. The shear rate sufficient for inducing LC phase transition in the brush decreases with approaching the temperature of LC transition in unperturbed brush.

Conclusions

In this review we collected the main results of long-term theoretical investigations of LCP brushes. We focused on general features typical of the systems addressing readers to previous publications for all the details. We conclude that LC phase

transition occurs as collapsing of the brush and microphase segregation is typically observed. These results have been obtained for all models considered in the observed studies. The effects are general since they are manifested under application of various methods of theoretical investigation, namely, analytical theory written for simple model of Alexander and de Gennes, numerical calculations in self-consistent field approximation of Scheutjens and Fleer, Brownian dynamics simulation. Therefore we believe that these features are characteristic of LCP brushes in general and the results of the reviewed theoretical studies could be helpful in organizing synthesis and experimental study of these complicated objects.

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