Spatial Self-organization of Comb Macromolecules

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Abstract—The properties and the self-assembly of single comb macromolecules in solution were studied. The elastic properties of a polymer chain with a high density of side chains forming a cylindrical brush were discussed, in particular, its persistence length was calculated. The cases of brushes with flexible and rigid side chains, as well as brushes with two types of incompatible side segments, were considered. It was shown that brushes with rodlike dangling chains have a higher rigidity. In addition, a comb macromolecule with the hydrophobic main chain and hydrophilic side chains was considered. Such a macromolecules in a selective solvent forms a globule with the hydrophobic core and a soluble shell. The specific feature of the globule is its ability to acquire nonspherical spatial forms. Problems related to the stability and transformation of globule shape are discussed in detail.

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INTRODUCTION

Polymer chains with a sophisticated architecture attract considerable attention of investigators both from the viewpoint of basic research because of the ability of such macromolecules to self-assemble and for solution problems in applied research when molecules of this kind can be used as structural units in the design of new engineering and functional materials. In this paper, we consider comb macromolecules, entities whose investigation has made great progress over recent decades. A comb macromolecule consists of a main chain or the backbone and long dangling side chains. The main chain and side chains can be both flexible and rigid (mesogenic) (Fig. 1). The presence of mesogenic groups in comb polymers leads to the possibility of LC ordering in their solution and melts. The combination of LC order and polymer viscoelasticity makes such systems promising for practical applications. Comb LC polymers have intensively been studied during recent decades. This refers as well to macromolecules composed of a flexible main chain with mesogenic side chains [1, 2].

In this paper, we will limit ourselves to the properties of single molecules in solution.

Important characteristics of comb polymers are the length of side chains, the grafting density, and the chemical nature of the main chain and the side chains. A difference in chemical nature between blocks that form the main chain can lead to their separation on the microscopic scale and, as a result, to the appearance of a great variety of spatial structures.

We will dwell upon two types of entities. The first type is a comb chain with a high grafting density having a cylindrical (bottlebrush) shape. Owing to the excluded volume interaction of side chains, bottlebrushes possess high rigidity and can form lyotropic liquid crystals. The other object of consideration is a globule formed by a long hydrophobic chain with hydrophilic side groups. Such a globule consists of the hydrophobic core and the hydrophilic shell composed of dangling side chains. We will analyze in detail the case of globule with a high surface density of side groups, at which its surface experiences structuring.

THEORY OF CYLINDRICAL POLYMER BRUSHES

Consider comb polymers with a high density of side groups. The comb-shaped chain forms a cylindrical brush when the Gaussian size of its side chains exceeds the distance between two-successive chain grafting points on the backbone (Fig. 2). Cylindrical brushes were first synthesized via radical polymerization of macromonomers as described in [3–5]. Further studies revealed that solutions of cylindrical brushes are amenable to LC ordering [6], a fact that indicates the presence of high rigidity in the brushes. This fact was also corroborated by the dependence of the radius of gyration of coils formed by brushes on the molecular mass of side chains, as obtained on the basis of light scattering data [7–11].

The first theoretical studies on cylindrical brushes, performed by Birshtein et al. [12] and Fredrickson [13], were based on the scaling concept. Birshtein et al. [12] assumed that the brush rigidity due to excluded-volume interaction of side chains is low because of reparation-
Going of side groups from the concave to the convex side during bending. On the basis of this assumption, it was concluded that the persistence length $\lambda$ of a brush is approximately equal to its diameter; i.e. $\lambda \approx D$. As follows from the theory of rigid-chain polymers [14], the formation of LC solutions is impossible in this case. More detailed calculation performed in [13] for the case of good solvent showed that the excluded volume interaction of side segments actually leads to a stronger dependence of the persistence length of the brush on the side-chain molecular mass $M$ and is described by the scaling law $\lambda \propto M^{15/8}$. On the basis of the facts that the brush diameter in a good solvent increases with an increase in $M$ according to the $D \propto M^{3/4}$ law and the ratio of the persistence length of the brush to its diameter is large for sufficiently large side chains; i.e. $\lambda/D \sim M^{9/8} \gg 1$, the feasibility of LC ordering in solution of polymer brushes was predicted. This result was later confirmed by the direct observation of lyotropic behavior [6]. At the same time, the scaling concept was ineffective in obtaining numerical values for the proportionality factor between the persistence length and the molecular mass. The influence of the rigidity of side chains on the brush persistence length also remained an open question.

Cylindrical brushes have been quite extensively studied by means of computer simulation [15–21]. Rouault and Borisov [15] performed a Monte Carlo study of comb polymers. They revealed that the brush rigidity increases as a result of excluded-volume interactions of side chains, a finding that is in qualitative agreement with the results of the scaling theory. More detailed numerical simulation studies of cylindrical brushes were reported in [16–19]. These investigations showed a slower rise in the persistence length depending on the molecular mass than predicted by the scaling theory. The disagreement can be explained in terms of the length of side chains, which was too short for the dependence to experience the asymptotic behavior. Thus, the problem of consistence of the scaling theory with the results of numerical simulation rests on a more accurate quantitative determination of the dependence of the persistence length on the molecular mass. In part, this problem was tackled by Feuz et al. [22] via numerical solution of equations of the self-consistent field theory. The cited authors showed that the numerical prefactor in the equation relating the persistence length to the molecular mass of side chains is very small. A similar result was obtained in an earlier study [23], in which the persistence length of a cylindrical brush was analytically calculated on the basis of the mean-field approximation. The dependence of the persistence length on the rigidity of side chains was studied in [18, 19]. It was found that the brush rigidity increases with an increase in the rigidity of side chains.

Much attention has been given to polymer brushes adsorbed on the surface [24–27]. The specific feature of such two-dimensional brushes is their inclination toward spontaneous bending [25]. This effect was explained on the basis of analytical calculations [24, 26] and was confirmed by numerical simulation [27].

In the present study, we will consider the elastic properties of cylindrical brushes with flexible and rod-like side groups as well as brushes with two types of side groups in terms of the mean-field approximation. General approaches to investigation of polymer brushes on the basis of statistical physics methods and an analogy between the extended-chain conformation and a trajectory of a classical particle in an external field were developed in [28–32]. In the present paper, these approaches are applied to cylindrical brushes, includ-