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Persistence Length of Comblike Polymers Strongly Adsorbed on a Flat Surface

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The high stiffness of densely grafted comblike macromolecules in solutions is known to be related to intramolecular interactions of the side chains. However, from the very first theoretical studies of this matter, there were not univocal predictions concerning dependence of the persistence length of the macromolecule on the side chain length. Using scaling theory with a coarse-grained description of the average conformations of the macromolecules on a large length scale (a wormlike chain with an effective (apparent) contour length, persistence length, and a cross-sectional thickness), Birshtein et al.[1] found that the persistence length λ of the macromolecule in a good solvent is proportional to its thickness D and scales as $\lambda \sim D \sim n^{3/4}$, where n is the number of segments of the side chain. Such a dependence was explained by the interplay of "bare" stiffness of the backbone and repulsive interactions of the side chains. A much stronger dependence of λ on n, $\lambda \sim n^{15/8}$, was predicted by Fredrickson[2] via scaling analysis, suggesting that strong intermolecular repulsion of the side chains induces rigidity of the macromolecule on large length scales. The follow-up theoretical studies did not clarify this discrepancy. Most of the computer simulations[3−5] supported the theory by Birshtein et al., whereas the mean-field calculations[6,7] were in favor of Fredrickson's theory. Experimental studies of comblike macromolecules in solutions, which were performed by different scattering techniques,[8−10] relate to the theories in the sense that the macromolecules elongate with the increase of the length of the side chains. However, the form of the dependence of λ on n was not analyzed in these studies.

A very demonstrative way of calculation of the persistence length concerns macromolecules strongly adsorbed on a flat substrate: the AFM micrograph of the ensemble of macromolecules gives full information about their statistics.[11,12] Sheiko et al.[13] recently analyzed conformations of comblike macromolecules with the same number-average degree of polymerization of a poly(2-hydroxyethyl methacrylate) backbone, $N_n = 2150 \pm 100$, and different degrees of polymerization of poly(*n*-butyl acrylate) (pBA) side chains ranging from $n = 12 \pm 1$ to $n = 140 \pm 12$. They found that the persistence length of the molecules adsorbed on mica scales as $\lambda \sim n^{\nu}$, $\nu = 2.7 \pm 0.2$. This value of the exponent is much higher than that predicted theoretically.[1,2] Below we propose a model which brings a theory and the experiment together.

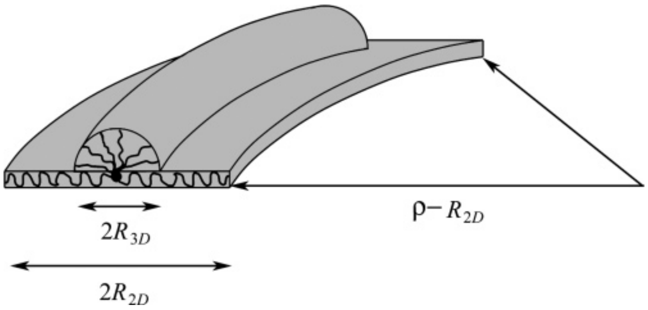

Figure 1. Schematic representation of a segment of the brush molecule strongly adsorbed on a flat surface.

In contrast to solutions, conformation and flexibility of adsorbed comblike (brush) macromolecules are mainly controlled by (i) the strength of interactions of the side chains with the surface and by (ii) the symmetry of left−right distribution of the side chains with respect to the backbone in the case of their strong attraction to the surface.[11,12,16,17] If the brushes are deposited on a solid−air surface (the air is known to be a poor "solvent" for polymers), the strength of interaction of the molecules with the substrate can be characterized in the terms of the spreading coefficient S which is a combination of substrate−air (γ_{sa}), substrate−polymer (γ_{sp}), and polymer−air (γ_{pa}) tension coefficients, $S = \gamma_{sa} - \gamma_{sp} - \gamma_{pa}$. Positive values of S correspond to the spreading of the molecules on the surface. Therefore, one can say that the higher S, the stronger attraction to the surface. In the case of the brushes with pBA side chains on mica, most of the side chains are flatten on the substrate and form practically a monomer thick layer while the rest of them form elevation around the backbone.[11−13] Therefore, a two-body model of the adsorbed brush molecule, comprising a two-dimensional layer and semicylindrical core (an analogue of sombrero-like structure of adsorbed star polymers[14]), Figure 1, seems to be reasonable for theoretical analysis. A local distribution of the side chains with respect to the backbone in 2D layer is determined by initial conformation of the brush in the solution. If the molecule is adsorbed from a good solvent, one can expect that the distribution is close to the symmetric one. Indeed, the brush in the solvent has an elongated conformation due to the high persistence length. Assuming that the adsorption process is very fast ("instant"), the fractions of left and right side chains in 2D can be considered as "projections" of the fractions in 3D. If the molecule has a globular conformation in the solution, strong adsorption may lead to the formation of pancake-like globule with a curved conformation of the molecule. This conformation is expected to have locally asymmetric distribution of the side chains. Below we will analyze bending modulus (persistence length) of the 2D layer with symmetric distribution of the side chains, although the bending moduli of the symmetric and asymmetric layers are close to each other.[17] Owing to incompatibility of polymer with the air, we assume that monomer units of the brush are densely packed.

Let us consider a brush molecule with flexible side chains grafted to each segment of the backbone. The numbers of the segments in the backbone and the side chain are N and n, respectively, $N \gg n$. Each segment of the brush has the same linear size, a, and excluded volume, $v \approx a^3$. Denote by $\phi = N_{2D}/N$ the fraction of the side chains forming the 2D layer. These chains are strongly stretched. From the dense packing condition, we can find that the end-to-end distance of the 2D side chains, R_{2D}, scales as $R_{2D} \approx an\phi/x$, where $x = L/aN \leq 1$ is the ratio of the apparent length of the brush, L, to the contour length of the backbone, aN. The elastic free energy of the 2D side chains per unit length of the brush can be estimated using the

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conventional Flory form:

$$\frac{F_{2D}^{(0)}}{k_B T} \approx \frac{N_{2D} {R_{2D}}^2}{L a^2 n} \approx \frac{n}{a}\left(\frac{\phi}{x}\right)^3 \qquad (1)$$

Despite the strong stretching of the 2D chains, this result coincides with that of the scaling approach (excluding the case of nearly full stretching). Let us imagine the stretched chain as a row of blobs of the size ξ. Each blob contains g segments which do not "feel" the stretching, i.e., $\xi \approx a g^{1/2}$. Then the elastic free energy per one chain is estimated as the number of blobs $n/g \approx {R_{2D}}^2/a^2 n$, where the dense packing condition, $R_{2D}\xi \approx a^2 n$, is used. Furthermore, the linear dependence of $F_{2D}^{(0)}$ on n, eq 1, remains valid even in the case of nearly full stretching, if we use the Langevin function for the description of nonlinear dependence of the end-to-end distance on the applied dimensionless force p,[11] $R_{2D} = an(\coth p - 1/p)$. Within this approach $F_{2D}^{(0)}/k_B T \approx n\phi[p \coth p - 1 - \ln(\sinh p/p)]/(ax)$[11] and in the limit of nearly full stretching ($\phi \approx x \approx 1$, $p \gg 1$), $F_{2D}^{(0)}/k_B T \approx n/a$. Thus, one can assume that the elastic free energy (1) is valid for any stretching of the side chains.

To find the persistence length of the brush, we use the scaling arguments. Taking into account that the persistence length is proportional to the bending modulus of the molecule (an additive parameter), let us consider the energy of small bending of the 2D layer and the semicylindrical core of the brush. Small bending of the 2D layer without desorption of the side chains (ϕ = constant) does not change the interfacial energy (the line tension is negligible), and the increase of the free energy is connected with the stretching of the side chains. Therefore, $F_{2D}^{(0)}$ is the only scale of the free energy of unbent 2D layer which changes at the bending. For an infinitely long 2D layer, the only length scale is the width $\sim R_{2D}$. Therefore, the free energy of small bending can be written as[15]

$$F_{2D}(\rho) \approx F_{2D}^{(0)}\left(1 + \frac{{R_{2D}}^2}{\rho^2}\right) \qquad (2)$$

where ρ is the curvature radius, $\rho \gg R_{2D}$ (Figure 1). If the side chains are allowed to be desorbed and readsorbed at the bending, the persistence mechanism of flexibility is violated and spontaneous curvature occurs.[12,18−20] However, to achieve this condition (at least for the brushes with pBA side chains on mica), very strong external forces are needed.[12] The thermal energy of strongly adsorbed side chains at room temperature is too small to overcome their strong attraction to the surface and induce flipping with respect to the backbone. Thus, the fraction of "left" and "right" side chains is assumed to be fixed at bending. Equation 2 means that the contribution of the adsorbed layer to the persistence length of the brush is[21] $\lambda_{2D} \approx F_{2D}^{(0)} {R_{2D}}^2/k_B T \approx a n^3(\phi/x)$.[5] Note that proportionality $\lambda_{2D} \sim n^3$ is also found for the 2D brushes with repulsive interactions between the side chains.[17] Furthermore, this result is a demonstration of the general law: the bending modulus of a thin plate (an analogue of our 2D layer) is proportional to the cube of its thickness.[15]

Similar arguments can be used for the estimation of the contribution of the 3D core. The dense packing condition of monomer units in the core determines the stretching of the side chains, ${R_{3D}}^2 \approx na^2(1 - \phi)/x$. The elastic free energy of the nonadsorbed side chains is $F_{3D}^{(0)}/k_B T \approx N_{3D}{R_{3D}}^2/(La^2 n) \approx (1 - \phi)^2/(ax^2)$, so that $\lambda_{3D} \approx F_{3D}^{(0)}{R_{3D}}^2/k_B T \approx an(1 - \phi)^3/x^3$. The total persistence length of the adsorbed brush is

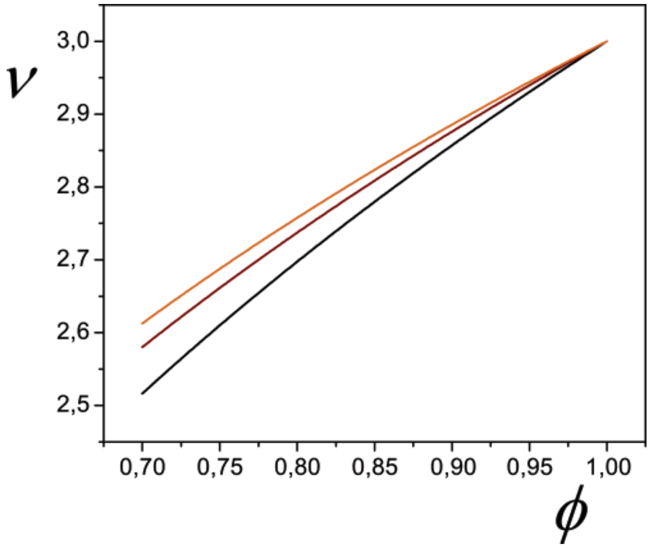

Figure 2. Effective exponent ν as a function of the fraction of adsorbed side chains, ϕ, at various values of the number of segments of the side chains, n: $n = 40$ (black), 70 (wine), and 100 (orange).

$$\lambda = \lambda_{2D} + \lambda_{3D} \approx n^3\left(\frac{\phi}{x}\right)^5 a + n\left(\frac{1 - \phi}{x}\right)^3 a \qquad (3)$$

Note that the parameters ϕ and x are controlled by the spreading coefficient.[11] For example, most of the side chains are strongly adsorbed on the surface, $\phi \approx 1$, and the backbone is close to the full stretching, $x \approx 1$, at high values of S. In this case the persistence length of the brush attains the maximum value, $\lambda \approx n^3 a$. The fraction ϕ decreases with reduction of the spreading coefficient. This is accompanied by a thickening of the 3D core and by a shrinkage of the apparent length of the molecule.[22] Let us estimate the maximum degree of shrinkage of the contour length at the condition that the molecule still has an elongated conformation. It occurs if the fraction of the 2D side chains is very small, $\phi \ll 1$, but nonzero, so that the chains are still able to prevent formation of a hemispheric globule.[22] In this case the contribution of the 2D chains to the total free energy is negligible compared to that of the 3D chains. The length of the brush in this regime is determined by a balance of two factors: (i) the elastic energy of the side chains that tends to elongate the backbone up to the maximum value and (ii) the polymer−air interfacial energy that tends to shorten the molecule. The corresponding free energy

$$\frac{F_{3D}}{k_B T} \approx N\frac{{R_{3D}}^2}{a^2 n} + \gamma_{pa} R_{3D} L \approx N\left(\frac{1}{x} + \bar{\gamma}_{pa}\sqrt{nx}\right),$$

$$\bar{\gamma}_{pa} \equiv \frac{\gamma_{pa} a^2}{k_B T} \sim 1 \qquad (4)$$

has the minimum at $x \approx 1/n^{1/3}$ and the thickness of the molecule $R_{3D} \approx an^{2/3}$. So, the degree of shrinkage of the contour length of the brush molecule in the regime of weak adsorption depends on the length of the side chains. Setting $\phi \approx 0$ and $x \approx 1/n^{1/3}$ in eq 3, we get $\lambda \approx n^2 a$. Therefore, if we approximate the dependence of the persistence length of the adsorbed brush molecule on the side chain length n (3) by the power function $\lambda \approx n^\nu a$, the exponent ν has to belong to the interval $2 \leq \nu \leq 3$. Taking into account that the backbone is completely stretched at high values of the fraction of the adsorbed side chains ($x \approx 1$ at $\phi \approx 0.7-1$[11]), one can find a weak (logarithmic) dependence of ν on ϕ and n, $\nu \approx 3 + 5 \ln \phi / \ln n + (1 - \phi)^3/(\phi^5 n^2 \ln n) + ...$, $n \gg 1$, which is represented in Figure 2. Therefore, considering ϕ as a fitting parameter, we can obtain the value of the exponent measured in ref 13. Assuming that the set of the values n is finite (as in the experiment), we can take the average value of ν. For example, taking $\phi = 0.78$ and calculating ν for $n = 40$, 70, and 100 (Figure 2), we get the average value $\bar{\nu} \approx 2.7$ with a small enough error.

In conclusion, we demonstrate that the persistence length of the adsorbed brush molecules has stronger dependence on the side chain length compared with the case of the brush molecules in solutions. The persistence length is controlled by the fraction of the adsorbed side chains: the higher the fraction, the larger the persistence length. Considering the fraction of the adsorbed side chains as a fitting parameter, we obtain quantitative agreement with experimental data.

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