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Unusual conformation of molecular cylindrical brushes strongly adsorbed on a flat solid surface

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Abstract. Conformational properties of comb-like polymers strongly adsorbed on a flat solid surface were investigated using computer simulation and scanning force microscopy. The computer simulation showed that the macromolecules with asymmetric distribution of the side chains relatively to the backbone are effectively in a collapsed state even under conditions of a good solvent. They formed peculiar helical superstructures which could be observed by scanning force microscopy of cylindrical brushes of polymethylmethacrylate on mica.

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1 Introduction

Recently, different synthetic strategies have been developed to prepare comblike polymers with a high density of linear side chains [1–5]. One might call this type of polymers "bottle-brushes" or cylindrical brushes as the radius of curvature is determined by the brush length. Both theoretical analysis and computer simulations report on the enhancement of the persistent length of macromolecules caused by steric repulsion between the side chains [6–11]. The competition between the entropic flexibility of the main chain and the excluded volume interaction of the side chains results in many interesting properties such as lyotropic ordering [12], axial contraction of the main chain [13,14], and microphase segregation [15,16].

Macroconformation and flexibility of molecular brushes are expected to change considerably when the brush molecules are adsorbed on a flat solid substrate. The system becomes essentially two-dimensional when each monomer unit gets in contact with the surface. The strong adsorption prevents overlapping of the side chain and induces in-plane directionality of the excluded volume interactions. Also the symmetry of the system is changed from the uniaxial symmetry of a cylindrical brush in solution towards plane symmetric distribution of the side chains in a strongly adsorbed brush. In this case, the macroconformation can strongly depend on the relative number φ of the side chains at the opposite sides of the main chain. In this paper, we report on the unusual configurational behavior of strongly adsorbed molecular brushes using the so-called cellular-automaton-based simulation technique and the scanning force microscopy (SFM).

2 Computer simulation

On the basis of the lattice bond-fluctuation model (BFM) [17] and the cellular-automaton-(CA-) based simulation techniques [18,19], we have studied 2d molecular cylindrical brushes consisting of a backbone (main) chain of N_b monomeric units linked with n side chains of N_s monomeric units; the total number of monomers in the macromolecule is $N = N_\mathrm{b} + nN_\mathrm{s}$. The computational method used in the present study is similar to the simulation scheme, maximally discretized molecular dynamics (MDMD), first proposed by Colvin *et al.* for investigation of lattice gases [20,21]. A polymer chain is represented by a sequence of consecutive beads (monomers) connected by effective bonds. In the BFM, each monomer occupies 2^d sites of square ($d = 2$) lattice [18]. Double occupancy is excluded. Chain crossings are prohibited with a proper choice of the maximum separation, $b_\mathrm{max} = \sqrt{13}$, of connected monomers i and $i+1$ [17]. Thus, the bond length can range from $b_\mathrm{min} = 2$ to $b_\mathrm{max} = \sqrt{13}$ in units of the lattice spacing. We consider particles moving on a square lattice with unit velocity $\mathbf{v}_\alpha$ in direction α ($\alpha = \pm x, \pm y$) between a given lattice cell occupied by particle i

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and one of its four nearest neighbors. Initial velocities are chosen randomly. The changes in particle velocities are caused by "elastic collisions" between pairs of particles i and j. The collisions take place if

$$\begin{cases} r_{ij} < 2 & \text{for all pairs } i \text{ and } j \\ r_{ij} > b_{\max} & \text{when } i \text{ and } j \text{ are chain neighbors} \end{cases} \tag{1}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\mathbf{r}_i$ and $\mathbf{r}_j$ are the corresponding position vectors. The collision laws of the discrete coarse-grained model give the transition rules for the internal states of each cell occupied by particles. The choice of the collision laws is somewhat arbitrary. We use the following highly simplified collision law: $\mathbf{v}_i \Leftrightarrow \mathbf{v}_j$, for any two colliding particles i and j. In other words, the motion of the particles is such that, if their relative positions do not satisfy the constraints (1), the particles move freely; in the opposite case, elastic collision takes place between the corresponding pair of particles and results in interchanging of their velocities. At each time step the particles attempt to move in the corresponding directions; whereas the trajectories between collisions are straight lines. When the collision occurs, the velocities of the two colliding partners relieve one another, but the particles are not moved until the next time step. In addition, each time the particle makes an attempt to move its velocity changes randomly with a certain probability γ. In calculations described below, γ was chosen to be 0.1.

The length of the main chain was varied from 32 to 2048 units. The side chains of lengths $N_{\mathrm{s}} = 1{-}48$ were considered. The grafting density is given by $\sigma = n/N_{\mathrm{b}}$. The maximum value $\sigma = 1$ corresponds to a structure where each backbone monomer is linked to one side chain. The main and side chains are considered as 2d self-avoiding walks (SAW). This means that the solvent surrounding the macromolecule is good (athermal) for all monomers. The starting configuration corresponded to a fully extended chain in the (x, y) plane. Depending on the total number of monomers, between 5×10^6 and 7×10^6 time steps were necessary to obtain a completely equilibrated configuration. After equilibration, the simulation was carried out during time intervals ranged from 5×10^6 to 2×10^7 time steps. The results are expressed in internal units: lengths are measured in lattice constants, and time, t, is measured in units of time steps.

For 2d cylindrical brushes, where all side chains are located on the one side of the backbone, we find an unusual behavior of chain dimensions as a function of backbone length. It turns out that the 2d bottle-brush SAW (*i.e.*, the chain with repulsive interactions between monomers) behaves like a typical globular structure in a bad solvent. To illustrate this effect, we present in Figure 1 the root-mean-square radius of gyration R_{g} of the backbone with smallest side chains, $N_{\mathrm{s}} = 1$, grafted at maximum one-sided density, $\sigma = 1$. From these data, it follows that the value of R_{g} scales with N_{b} as $R_{\mathrm{g}} \sim N_{\mathrm{b}}^{0.553 \pm 0.010}$. The exponent $\nu = 0.553$ is significantly smaller than the excluded volume exponent $\nu = 3/4$ known for 2d SAW's [22]. In fact, this exponent is very close to 1/2, the value which is characteristic for the unperturbed chains without excluded volume interactions or for 2d chains in collapsed (globular) state [22]. The same findings are correct for any other $n > 0$ and $\sigma > 0$. Note that in the case of sufficiently long 3d comblike macromolecules our simulation [19] predicts that the critical exponent, governing the mean size of the main chain as a function of its length, remains unchanged from its value ($\approx 3/5$) known for a 3d self-avoiding walk.

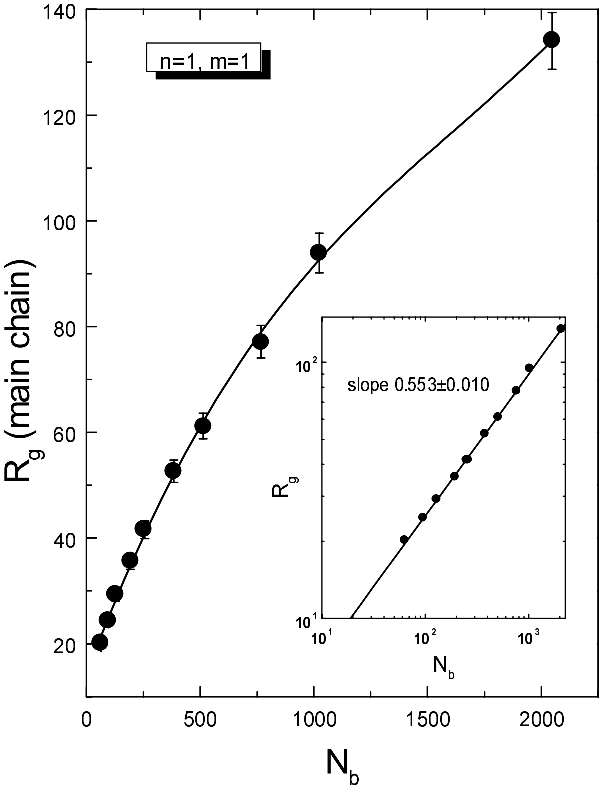

Fig. 1. Radius of gyration of the main chain of the 2d bottle-brush structure, R_{g}, as a function of main chain length, at $N_{\mathrm{s}} = 1$ and $\sigma = 1$. The value of R_{g} is measured in units of lattice spacing.

To study the local conformational structure of 2d comblike polymers, we define the so-called local fractal dimensionality (LFD) as

$$\mathrm{LFD}_k = \frac{\ln[k/(k-1)]}{\ln(\langle R_k^2 \rangle / \langle R_{k-1}^2 \rangle)^{1/2}},$$

where $\langle R_k \rangle$ is the mean-square distance between the end points of a chain sequence consisting of k monomers along the chain. The LFD represents the extent to which the chain is winding. If the chain is straight line, then $\mathrm{LFD}_k = 1$, whereas for a freely jointed noninteracting chain, $\mathrm{LFD}_k = 2$ for all k. In the intermediate regime, where the chain with excluded-volume interactions behaves as a 2d SAW, we have $\mathrm{LFD}_k = \nu^1 = 4/3$. Figure 2a shows a plot of R_{k}, the root-mean-square distance between end monomers i and j along the main chain, as a function of $k = |i - j|$ for three different N_{b}'s. We find

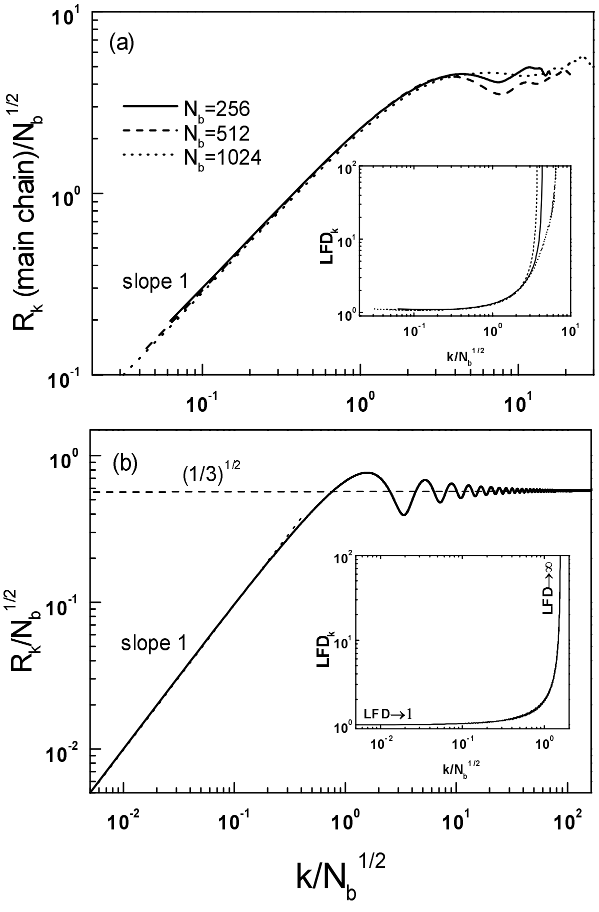

Fig. 2. (a) The value of $R_k/N_\mathrm{b}^{1/2}$ as a function of $k/N_\mathrm{b}^{1/2}$ for the main chain of the 2d bottle-brush structure for different values of N_b, at $N_\mathrm{s} = 1$ and $\sigma = 1$. The insert: the LFD function *vs.* $k/N_\mathrm{b}^{1/2}$. (b) The value of $R_\mathrm{k}/N_\mathrm{b}^{1/2}$ as a function of $k/N_\mathrm{b}^{1/2}$ for the 2d regular lattice spiral of infinite length. The insert: the LFD function *vs.* $k/N_\mathrm{b}^{1/2}$.

that the ratio $R_k/N_\mathrm{b}^{1/2}$ is a universal function of scaling argument $k/N_\mathrm{b}^{1/2}$, that is, $R_k = N_\mathrm{b}^{1/2} f(k/N_\mathrm{b}^{1/2})$. For the local fractal dimensionality, one has $\mathrm{LFD}_k = 1$ at small $k/N_\mathrm{b}^{1/2}$ and $\mathrm{LFD}_k \to \infty$ at large enough values of $k/N_\mathrm{b}^{1/2}$. This means that the backbone chain behaves as a straight line on a small length scales and becomes tightly twisted on large length scales. Such a behavior corresponds to a fractal object having a helical shape. To illustrate this in more detail Figure 2b depicts the same dependencies but obtained for an ideal two-dimensional helix constructed from the infinite number of sites, N, of a square lattice with unit spacing. In this case, the exact solution for the scaling function $f(k/N_\mathrm{b}^{1/2})$ is characterized by $\mathrm{d}f(x)/\mathrm{d}x = 1$ at $x \to 0$ and $f(x) \to 3^{-1/2}$ for large x. When the value of x increases, $f(x)$ exhibits a dumped oscillatory behavior. The LFD function, defined as $\mathrm{LFD}_k = \mathrm{d}\ln k/\mathrm{d}\ln R_k$, shows features similar to the 2d molecular brushes.

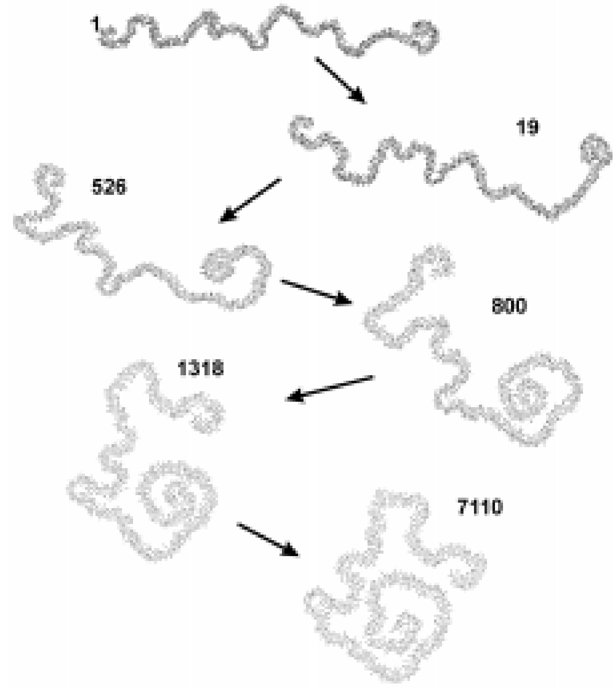

Fig. 3. Snapshot pictures of the strongly adsorbed (2d) bottle-brush structure consisting of the 256-unit main chain and the 10-unit side chains grafted at $\sigma = 1$ and $\varphi = 0.4$, where φ is the relative number of side chains, located at one of the sides of main chain. Configuration arising from fully extended state to a helical configuration after 1318000 time steps. The corresponding time steps (×1000) are indicated next to the snapshot pictures.

Thus we conclude that the equilibrium conformation of 2d comblike polymers is nothing but the tightly wound helix. Snapshots in Figure 3 illustrates the kinetics of the winding process of a brush molecules containing 40% of the side chains at one side and 60% at the other side of the backbone, *i.e.* $\varphi = 0.4$ (see below). The initially stretched brush molecule starts to wind at both ends, while at later stages one of the ends prevails and results in either left-hand or right-hand helix.

This behavior depends on the relative number of the side chains located on the opposite sides of the backbone. We use abovementioned parameter $\varphi = n_i/n$ to characterize the asymmetry of the side chain distribution, where n_i is the number of the side chains located at one of the sides of the main chain and consequently $n - n_i$ is the number of the side chains located at the opposite side. The value of φ was varied between 0 and 0.5. At $\varphi = 0$, all side chains are at one side of the backbone. This case was considered in Figures 1 and 2. The other limiting case $\varphi = 0.5$ corresponds to random orientation of the side chains with respect to the backbone, with an equal number of the side chains at either of sides. At $\varphi > 0$, the conformational properties were averaged over different side-chain distributions ($\sim 10^2$). We have found that the mean backbone size R_g is an increasing function of φ, as it can be seen from Figure 4. However, our simulation

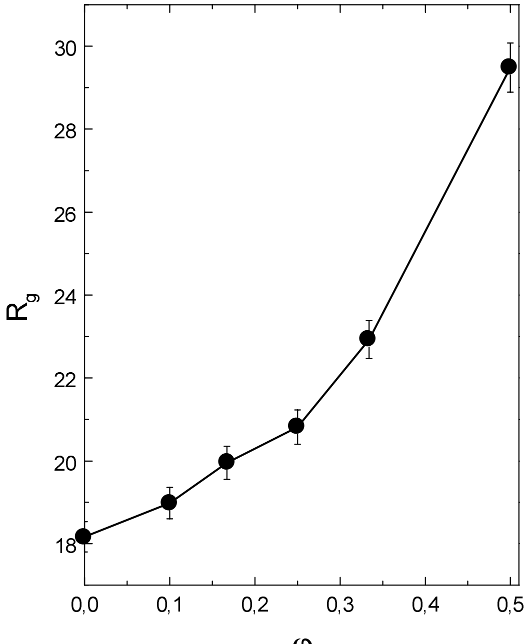

Fig. 4. R_{g} as a function of φ, at $N_{\mathrm{b}} = 60$, $N_{\mathrm{s}} = 4$ and $\sigma = 1$, where φ is the relative number of side chains, located at one of the sides of main chain.

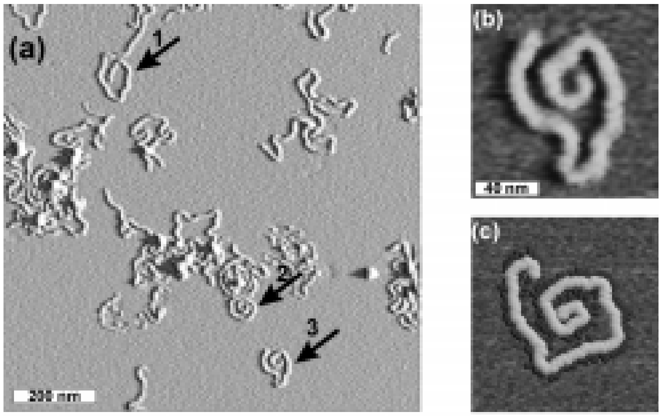

Fig. 5. (a) SFM micrograph of individual cylindrical brushes lying flat on the mica surface. The arrows show one of the typically observed conformations – 2d helices of tightly winded cylindrical brushes. (b) Zoomed image of molecule 3 in (a). (c) Typical snapshot of the simulated 2d bottle-brush structure consisting of the 128-segment main chain and the 4-segment side chains grafted at $\sigma = 1$ and $\varphi = 0.1$.

shows that long enough 2d comblike polymers form the helical conformation at any $\varphi < 0.5$, though the time needed for equilibration increases with increasing φ.

It should be noted, that the $\sqrt{8}$ forbidden bond vector in 3d bond fluctuation model leads to an alteration of the excluded volume interaction that is no more correctly screened [23]. For highly grafted chains this can have some effect. While this problem does not appear in two dimensions, it must be kept in mind for three dimensional systems.

3 Scanning force microscopy

Unlike $\varphi = 0$, the case of $\varphi \approx 0.5$ is quite realistic and might occur upon random sequential adsorption of cylindrical brushes on a flat surface. Scanning force microscopy was employed to verify the hypothesis regarding plausibility of the helical conformation of cylindrical brushes in a 2d state. Molecular brushes were prepared by polymerization of poly(methylmetacrylate) (PMMA) macromonomers with a methacrylate end group by group transfer polymerization as described elsewhere [14]. The degree of polymerization could be as high as $N_{\mathrm{b}} = 10^4$, while the molecular mass of the macromonomer $M_{\mathrm{n}} = 2410$ g/mol corresponds to $N_{\mathrm{s}} = 24$. Thus, the resulting brushes consist of a long polymethylacrylate main chain and relatively short poly(methylmethacrylate) side chains grafted to each monomer unit of the backbone, *i.e.* $\sigma = 1$. To obtain macromolecules with a relatively narrow molecular weight distribution, the samples were fractionated by preparative size exclusion chromatography using tetrohydrofuran (THF) as a solvent. The fraction containing the largest molecules with $M_{\mathrm{w}} = 25 \times 10^6$ g/mol and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.4$ was chosen for the experiment.

The PMMA polymacromers were deposited from a dilute solution in chloroform by spincasting on a freshly cleaved crystal of mica. Chloroform is a good solvent for PMMA, while the polar surface of mica causes strong interaction with the polar methylmethacrylate units. In contrast to previous works [14,15], very dilute solutions (10^{-2}–10^{-1} g/l) in the low-boiling-point solvent were used to prepare single molecules rather than dense monolayers. Scanning force micrographs were recorded with a Nanoscope IIIa scanning force microscope (Digital Instruments) operated in the tapping mode at a resonance frequency of about 300 kHz. The measurements were performed at ambient conditions (in air, 50% RH, 23 °C) using Si probes with a spring constant of ≈ 50 N/m.

The resulting SFM image is shown in Figure 5a where the individual macromolecules are observed lying flat on the mica surface. Due to the strong interaction of PMMA with mica, the molecules are compressed towards the surface so that the width of the molecule $d_{\|} = 10 \pm 1$ nm measured parallel to the surface plane was significantly larger than their height of $d_{\perp} = 2.0 \pm 0.1$ nm. The width was estimated by deconvolution of the independently determined radius of the SFM tip $r = 8$ nm from the cross-sectional profile. Figure 5a displays different types of macroconformations which were vitrified by rapid evaporation of the solvent. One of the typically observed molecular conformations are the compact helix-like structures indicated by arrows. *E.g.*, the molecule indicated by arrow 3 (Fig. 5b) is very similar to those predicted theoretically and shown in Figure 5c. Although this coincidence is very remarkable, one cannot expect that all of the adsorbed brushes will adopt such conformation. The final conformation is controlled by the adsorption process depending on the molecular structure (degree of polymerization, side-chain length, grafting density), adsorption strength, the solvent quality, and the vapor pressure. Due to the fast evaporation of the solvent, it might take prohibitively long to achieve the equilibrium structure for large molecules strongly adhering to the substrate. Eventually, the helical conformation can be observed if the asymmetry of the side chain distribution relative to the backbone is sufficiently large (small φ) and the side chains are sufficiently long to wind the molecules during the short time interval of the adsorption event. The micrograph in Figure 5a shows that less than 10% of the adsorbed molecules were able to form the helix. The ongoing experiments are focused to control the adsorption process and the chemical structure of the brushes to approach the equilibrium state.

4 Conclusive remarks

The origin of such unusual molecular conformations is rather trivial. The excluded volume of the side chains induces the spontaneous bending of the chain, *i.e.*, the conformation corresponding to the minimum bending energy is not rectilinear. It is also interesting to note that the formation of the helix-like objects is observed in computer simulations for two-sided $2d$ comblike polymers at $\varphi = 0.5$ as well, provided that the chains grafted to each side of the backbone are characterized by different excluded volume interactions. In this case, by varying the quality of solvent (*i.e.*, the interaction between the corresponding side-chain monomers), one can change the direction of winding or unwinding. Actually, such a system represents a "molecular spring" which could act as a molecular nanodevice transforming chemical energy into mechanical.

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