Lateral Structure of a Grafted Polymer Layer in a Poor Solvent

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ABSTRACT: We have used atomic force microscopy (AFM) to study the lateral structure of end grafted poly(styrene) chains on a silicon substrate in air. As the grafting density is decreased, the chains are found to "clump" together into islands, resulting in a highly inhomogeneous monomer density with considerable portions of the substrate exposed to air. The transition from a stable homogeneous film to the clump formation is in agreement with recent theoretical simulations of polymer brushes in different solvent conditions. The islands are found to be interconnected by thin arms, which can be visualized as isolated chains stretching out on the substrate.

End grafted polymer layers have recently been the subject of intensive study both experimentally and theoretically.[1-4] This is mainly due to their outstanding technological importance in areas like colloidal stabilization, lubrication, adhesion, and chromatography. Theoretical interest on the other hand arises from the fact that the confinement of the chain ends leads to conformations qualitatively different from the free chain situation. While most of the investigations performed so far were concerned with the brush structure perpendicular to the grafting surface, it has only recently been pointed out that in-plane instabilities may occur under certain conditions when the polymer brush is exposed to a poor solvent environment. In Monte Carlo simulations, Lai and Binder observed lateral density inhomogeneities as the temperature was lowered sufficiently below the Θ temperature.[5] Yeung and co-workers investigated the lateral stability of polymer brushes utilizing the random phase approximation combined with a numerical mean field analysis.[6] They predict a "dimpling" of the brush in the poor solvent regime, with the separation and depth of the "dimples" depending on grafting density, solvent quality, and chain length. Finally, Grest and Murat have recently performed molecular dynamics (MD) simulations of polymeric brushes,[7] again revealing that in the poor solvent regime phase separation can occur between monomer-rich and monomer-poor domains as the grafting density is decreased. The very illustrative "snapshots" of their MD results show isolated agglomerations of polymer chains with some chains reaching out to the neighboring islands. Experimental studies have so far almost exclusively been concerned with the determination of the brush height and density perpendicular to the grafting surface. O'Shea and co-workers very recently reported a first study of the lateral properties of poly(ethylene oxide-*b*-styrene) diblock copolymers grafted to a mica surface.[8] They investigated the imaging capabilities of atomic force microscopy (AFM) under various solvent conditions. For the poor solvent regime they report features in qualitative agreement with the theoretical predictions quoted above.

In the present study, we investigate ultrathin layers of $Si(OH)_3$-terminated poly(styrene) (PS) ($N_{PS} = 1473$) spun onto Si substrates from a toluene solution. The film thickness as determined by ellipsometry amounted to 50(2) Å. In order to ensure enough mobility for the chain ends to reach the grafting surface, where they are chemically reacted, the samples were vacuum annealed at 170 °C for 3 days. Different grafting densities were obtained by dipping the samples in toluene for different times subsequent to film deposition and annealing. It was assumed that by this process grafted chains were removed from the surface in a random manner, thereby decreasing the grafting density. The number of chains removed was proportional to the duration of the dip. An alternate way of preparing a grafted film is the technique used in ref 6, where the end grafted chains are adsorbed from solution. In this case, the grafting density is controlled by the adsorption isotherm and therefore more difficult to control. In order to compare the results obtained by the two techniques, a second set of samples was prepared by dipping clean, native oxide covered Si substrates into dilute toluene solutions of the end-functionalized polymer (concentration approximately 1 mg/mL).

After washing, all samples were air-dried and studied with a Digital Nanoscope III atomic force microscope in the contact mode using a Si_3N_4 tip. To ensure reproducibility, multiple scans were taken from each sample surface. It was found that minimal damage to the surfaces occurred when the applied force was kept below 18 nN. Additional experiments were performed in a liquid cell with purified water acting as an alternative poor solvent. However, since water is known to hydrolyze and thereby weaken the grafting bond, the structures imaged in water were damaged after multiple AFM scans. The results of the initial scans in water resembled those taken in air, confirming that the poor solvent quality of air is indistinguishable from that of a liquid poor solvent, i.e. water. We shall therefore restrict ourselves to images taken in air for the reminder of this paper. Figure 1 shows AFM pictures of the spun cast PS films washed in toluene for various times. Initially, a continuous film is obtained with an average thickness of about 50 Å. Given a radius of gyration R_g of about 110 Å for a free PS chain of the respective molecular weight, this film thickness clearly indicates that the polymer brush is strongly compressed with the surrounding air acting as a poor solvent. The substrate surface is covered almost completely, and only a few isolated holes are observed.[9] On further removal of grafted chains however, the lateral structure of the film changes and a bicontinuous pattern is observed (Figure

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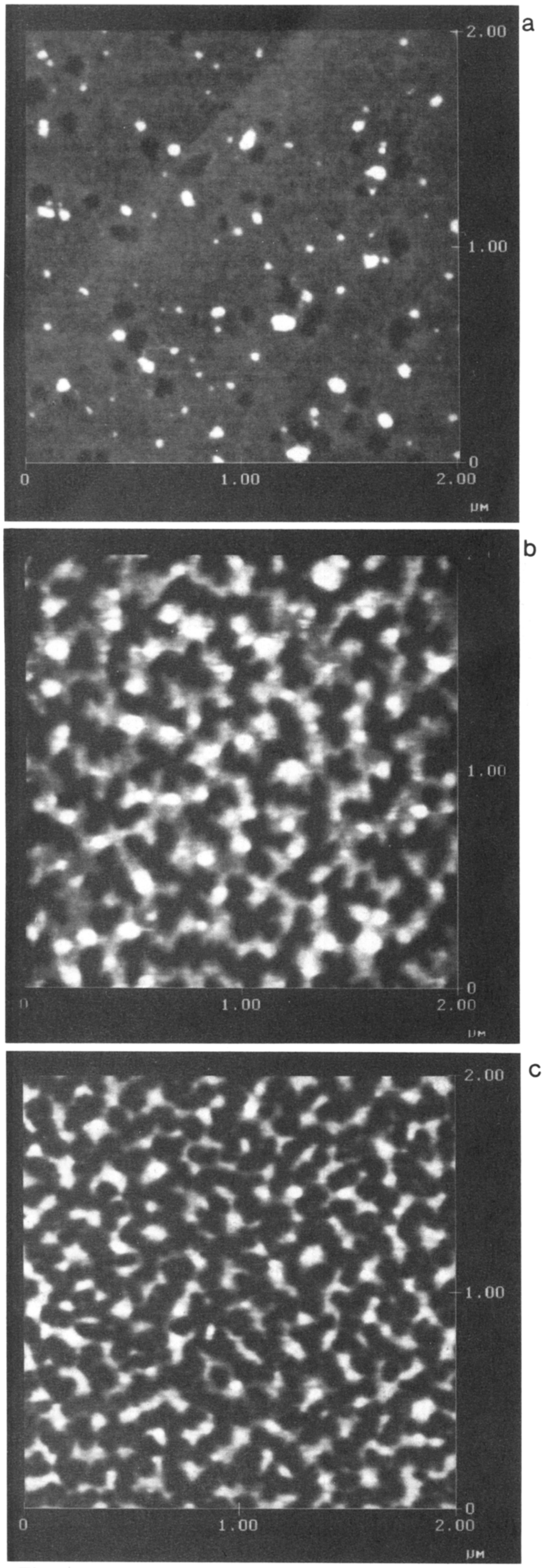

Figure 1. AFM images of $Si(OH)_3$ end-functionalized polystyrene grafted to a Si substrate: (a) after film deposition/ annealing; (b, c) after subsequent removal of chains by shear flow in toluene. Gray scale: 0–10 nm.

1b,c) with regions of high polymer density (approximately 50 Å in height) separated by almost polymer free regions on the substrate surface. This rather qualitative picture is in general agreement with the theoretical predictions;[5–7] i.e. for a given chain length one expects a phase transition between a continuous (one-phase) region at high grafting densities and a two-phase region at lower grafting densities, where domains of high polymer density are separated from an almost polymer free phase. As pointed out in ref 7, this phase transition should only be observable in a certain range of chain lengths N and grafting densities ρ and will not occur when either of the two parameters exceeds a certain maximal value.

For a more quantitative comparison with these predictions, it is therefore important to assure that the experimental situation falls in a (N, ρ) range that is comparable to the one studied by the computer simulations. In the MD simulations reported by Grest and Murat,[7] chains lengths ranged from 50 to 200 with grafting densities between 0.03 and 0.1 (in units of σ^{-2}, with σ being the average segment length). We may define a dimensionless scaling parameter x by comparing the typical dimensions of a polymer chain in a poor solvent with the average distance between grafting points $\rho^{-1/2}$, i.e. $x = N^{1/3}\rho^{1/2}$. In the MD simulations quoted above, x ranged between 0.6 and 1.8, with phase separation occurring in the low x regime (for short chains and low grafting densities) and a single, homogeneous phase in the regime of higher values of x. For our experimental situation, the average statistical segment length of PS and the aerial density of grafted chains is $\sigma_{PS} = 6.7$ Å and $\beta = 2 \times 10^{-4}$ Å^{-2}, respectively. Consequently, we can approximate a density of $\rho_{exp} = 0.01$ grafting points in an area $(\sigma_{exp})^2 = 45$ Å^2. With the degree of polymerization $N_{exp} = 1473$, we find $x_{exp} = 1.14$ for a 50-Å-thick uniform coverage of the substrate surface. Given the fact that the substrate surface is only partially covered as the grafting density is decreased, we find $x = 1.08$, 0.74, and 0.40 for the situations shown in Figure 1 with corresponding grafting densities of $\rho_{exp} = 0.0095$, 0.0065, and 0.0035, respectively. Although the actual values of N_{exp} and ρ_{exp} do not coincide with the situation studied in the MD simulations, the above scaling analysis justifies a comparison of the experimental findings with the MD results. The range of x_{exp} values estimated and the fact that the transition between a single homogeneous phase (Figure 1a) and a phase separated pattern (Figure 1b) occurs between $x_{exp} = 1.04$ and 0.74 are in fair agreement with the results of ref 7, where a similar transition is reported for a grafting density of 0.03 when the chain length is decreased from 100 to 50, corresponding to a change in x from 0.78 to 0.6. We shall point out, however, that given the uncertainties entering the above estimates, this comparison can be only semiquantitative. A detailed study of the proposed scaling prediction, i.e. a thorough investigation of the observed phenomenon as a function of molecular weight of the end grafted species, needs to be carried out and will be the subject of future work.

While the above discussion was primarily concerned with the large scale properties observed in the AFM experiments, it is instructive to investigate some small scale details of the island structure at low grafting densities. We illustrate this using a sample prepared by grafting from a dilute polymer solution rather than spin casting of the initial film. The sample has been carefully washed in pure toluene and dried in air in order to assure that both nongrafted polymer and solvent residues are removed prior to the AFM experiment. The AFM results obtained this way closely resemble the findings for the spun cast films. In Figure 2a, we show a high magnification detail for a sample with grafting density $\rho_{exp} = 0.0015$. In this low

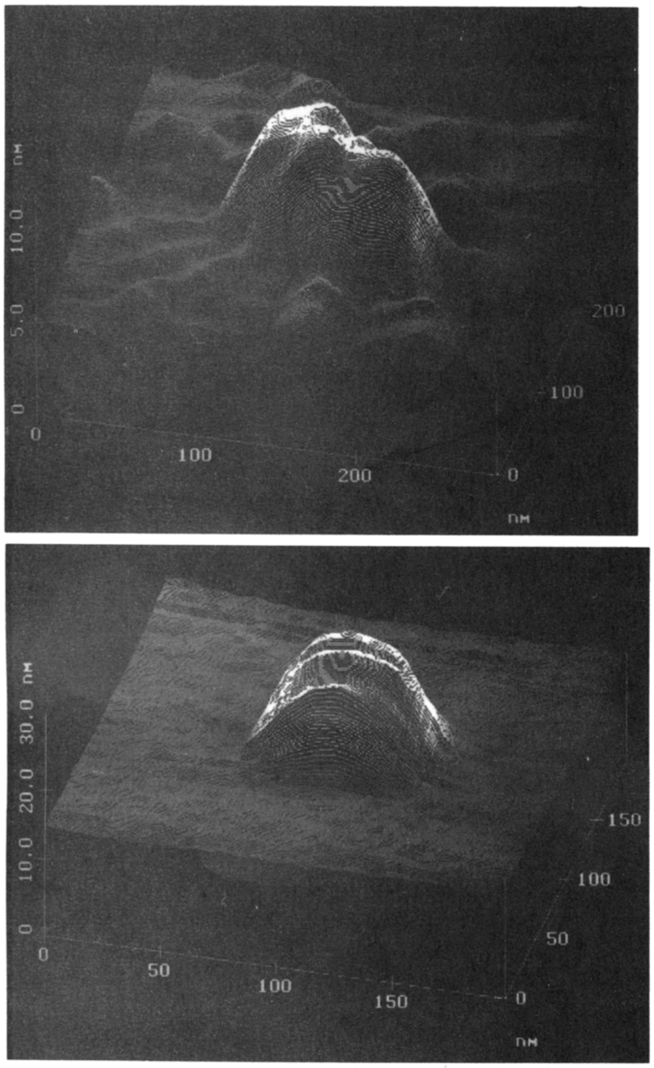

Figure 2. AFM images of Si(OH)$_3$ end-functionalized polystyrene grafted to a Si substrate from solution: (a, top) directly after solvent removal; (b, bottom) after annealing for 12 h at 160 °C.

grafting density regime, the polymer brush separates into isolated islands with large portions of the substrate uncovered. This again is in general agreement with the theoretical findings. Furthermore, we find that the surface of the islands is bumpy and the edges tend to have an octopus-like morphology with different "arms" reaching out to the neighboring islands. Far enough away from the center of the islands, the dimensions of these arms decrease to about 20 nm in width which is of the order of the radius of gyration of single PS chains of the respective molecular weight. The surface bumps are related to the dimpling instability found in ref 6. The arms can be visualized as originating from isolated PS chains stretching out on the surface. Both findings are in striking agreement with the MD results of ref 7 (see, e.g. Figure 1 in ref 7). We also tried to anneal these samples in order to find out whether the situation reached after solvent drying represents thermodynamic equilibrium (Figure 2b). From the figure we can see that the islands coalesced somewhat to form taller, smoothly rounded structures, reminiscent of the microdroplets observed in dewetting of thin polymer films.[10] The disappearance of the "bumps" is in qualitative agreement with the predictions of ref 6, where the surface instability becomes less probable as the grafting density is increased locally. The "arms" we believe retracted toward adjacent islands, where they can lower their energy by increasing the number of monomer–monomer contacts. A more detailed study of the kinetics involved in retracting the arms could possibly be used to study the diffusion of diluted chains on a surface. This however lies beyond the scope of this paper and shall be addressed elsewhere.

Finally, we shall address the question whether the patterns formed after removing the solvent represent thermodynamic equilibrium regardless of the method of preparation. We therefore spun cast another set of films on the Si surface which were initially smooth and of a total thickness corresponding to less than a monolayer coverage (thickness: 30 Å). These samples, which were not exposed to solvent, were then annealed together with the sample shown in Figure 2a. It turned out that the 30-Å film broke up to form an interconnected pattern similar to the one shown in Figure 1b for the sample of comparable grafting density. This observation suggests that the patterns produced after dipping in toluene solvent are due to breakup of the brush from lateral instabilities rather than inhomogeneous removal of the grafted chains in the toluene flow.

In summary, we have investigated the lateral structure of an end grafted polymer brush on a Si surface in a poor solvent. The results were found to be in quantitative agreement with recent theoretical investigations. A scaling argument was used to compare the experimental and theoretical results; future experiments will aim to investigate the suggested scaling behavior in more detail.

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(9) The isolated bright features on some of the AFM pictures originate from dirt particles that are observed quite often for various polymer samples studied in air. O'Shea and co-workers[8] reported similar features that vanished on addition of solvent, indicating soluble low molecular weight residues.
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