Surface Interaction Forces of Well-Defined, High-Density Polymer Brushes Studied by Atomic Force Microscopy

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Direct force measurements were made by atomic force microscopy (AFM) at surfaces of polymer brushes comprising low-polydispersity poly(methyl methacrylate) chains densely end-grafted on a silicon substrate by living radical polymerization. These brushes are characterized by an exceptionally high graft density. The AFM force measurements revealed that the repulsive force rapidly increased with decreasing separation in toluene. The equilibrium thickness of the brushes was found to be proportional to the chain contour length. This indicates formation of a homogeneous polymer layer with highly stretched graft chains. Unlike the previously reported results for lower density polymer brushes, longer brushes were more resistant to compression. It is believed that these are the first observations of "polymer brushes" in the true sense of the words.

Keywords: Atomic force microscopy / Living radical polymerization / Polymer brush / Steric repulsion

Polymers densely end-grafted on a solid surface will be obliged to stretch away from the surface, forming a so-called "polymer brush". Because of their important role in many areas of science and technology, e.g., colloid stabilization, adhesion, lubrication, tribology and rheology, polymer brushes in a solvent have been extensively studied theoretically and experimentally. Most of the polymer brushes experimentally studied so far were prepared by end-functionalized polymers or block copolymers with terminal group or one block selectively adsorbed on the surface. Such systems, however, had a rather low graft density due to the steric hindrance of preadsorbed chains. Theoretical analyses of polymer brushes with higher graft densities predict that the repulsive force steeply increases with increasing graft density. By the adsorption method, however, it is difficult to obtain such high graft densities. An alternative method is the graft polymerization starting with initiating sites fixed on a surface, but it usually results in a poor control of chain length and its distribution.

We firstly succeeded in applying a living radical polymerization technique to the graft polymerization and densely grafting low-polydispersity poly(methyl methacrylate) (PMMA)[1]. In this work, we have made an AFM study on the structure and interaction forces of such dense PMMA brushes in toluene[2]. The graft density σ was estimated to be as high as 0.4 chains/nm^2, which is one of the highest ever reported values, being an order of magnitude larger than those of the polymer brushes prepared by the adsorption method. The characteristics of the brushes are given in Table 1.

The interaction forces F were measured in toluene as a

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Scope of research

Basic studies have been conducted for better understandings of the structure/property or structure/function relations of polymeric materials and for the development of various types of polymers with controlled structure and/or novel functions. Among those have been the studies on (1) the mechanism and kinetics of "living" radical polymerization and its applications to the synthesis of well-defined polymers and copolymers of varying architecture, (2) the synthesis and properties of cellulose- and oligosaccharide-based functional polymers, and (3) the structure of polymer gels, ultrathin films and polymer alloys.

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Table 1. Characteristics of PMMA Brushes

code	d [a] (nm)	M_n [b]	M_w/M_n [b]
C1	12	23000	1.36
C2	20	35900	1.36
C3	44	70500	1.34
C4	87	121700	1.39
C5	102	171400	1.56

a) Thickness in dry state measured by ellipsometry.
b) Values for free polymers produced in the polymerization system.

function of separation D using AFM while the brushes were compressed by a silica sphere probe attached on an AFM cantilever. The measured force F can be reduced to the free energy G_f of interactions between two parallel plates according to the Derjaguin approximation, $F/R = 2\pi G_f$, where R is the radius of the probe sphere. Figure 1 shows the F/R vs D curves. We note that the true distance D between the substrate surface and the silica probe, which usually is difficult to define in AFM experiments, was successfully determined by AFM-imaging across the boundary of a scratched and an unscratched region of the sample surface. The most notable feature of the F/R vs D curves is a rapid increase of the repulsive force with decreasing D. The observed repulsive forces originate from the steric interaction between the solvent-swollen brush and the probe sphere.

The equilibrium thickness L_e of the solvent-swollen brushes was determined as the critical distance from the substrate surface beyond which no repulsive force was detectable (cf. Figure 1). The scaling and self-consistent mean field approaches predict that L_e varies like

$$L_e \propto L_c \sigma^{1/3} \quad (1)$$

where L_c is the contour length of the graft chain. This relationship was confirmed by other theoretical calculations as well as by some experimental data. In Figure 2, L_e is plotted against L_c on logarithmic scale, where L_c is the number-average value calculated from the M_n value. The figure gives a linear line with a slope of 0.95, confirming eq.1. It should be noted that the ratio of L_e to L_c in our system gives a nearly constant value, $L_e/L_c = 0.8$, independent of L_c. This indicates that in our system, the graft chains are highly stretched in toluene as compared with those prepared by the adsorption of block copolymers, in which the graft densities are much lower, e.g., $L_e/L_c = 0.3$.

Using the scaling approach, de Gennes derived the equation concerning the interaction force between two parallel plates with a "moderately dense" polymer brush layer, in which graft chains overlap each other but the volume fraction of polymer in the layer is still low. This predicts that the F/R value should be scaled by D/L_e for the polymer brushes with the same graft density. The results for the block copolymer brushes were reported to be nearly consistent to this scaling theory. Our system, however, was poorly represented by this scaling theory. This indicates that the graft density in our system is so high that the scaling theory is no more applicable. In the case of the shortest graft chain, the brush layer was compressible nearly to the dry thickness ($D/L_e = 0.3$). With increasing chain length, the scaled force curve becomes steeper, meaning that the brush layer becomes more and more difficult to be compressed. The system with the longest graft chain was compressible only to $D/L_e = 0.8$, which is about three times larger than the dry thickness. This strong resistance against compression must be characteristic of polymer brushes with an extremely high graft density.

In conclusion, we succeeded in preparing low-polydispersity PMMA brushes with an exceptionally high graft density. AFM force measurements revealed that these polymer brushes have properties quite different and unpredictable from the "moderately dense" polymer brushes previously studied. Most notably, the chains in these high-density brushes were highly extended, nearly to their full lengths, and highly resistant against compression. It is believed that these were virtually the first observations of the "real" polymer brush behavior.

References

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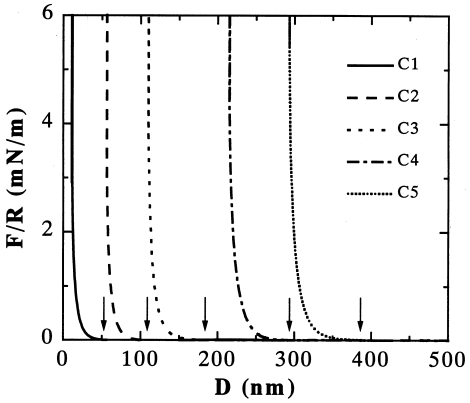

Figure 1. F/R vs D curves. The arrowheads indicate L_e.

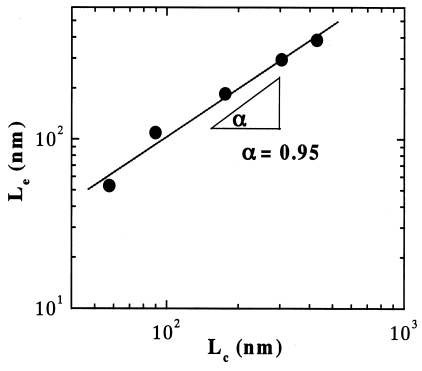

Figure 2. Plot of L_e vs L_c.