Atomic Force Microscopic Study of Stretching a Single Polymer Chain in a Polymer Brush

Shinpei Yamamoto, Yoshinobu Tsujii, and Takeshi Fukuda*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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ABSTRACT: We made direct force measurements by atomic force microscopy (AFM) to elucidate the elastic properties of a single polymer chain in a "semidilute" polymer brush in a good solvent (toluene in this study). A block copolymer brush comprised of low-polydispersity poly(methyl methacrylate)-*b*-poly-(4-vinylpyridine) (PMMA-*b*-P4VP) chains end-grafted on a silicon substrate was prepared by the surface-initiated atom transfer radical polymerization technique. The graft density of this brush (0.07 chians/nm^2) is high enough to form a semidilute polymer brush. The introduction of a short P4VP block at the free chain ends of a PMMA brush made it possible to selectively pick up the chain ends and stretch the PMMA chains by an AFM tip. Upon retraction of the AFM tip, discrete multiple attraction peaks were observed, each of which was attributed to the detachment of a single graft chain from the AFM tip. Each elastic response curve could be well-fitted to the wormlike chain (WLC) model, giving an estimate of the contour length L_c of the related single chain. These analyses revealed that the elastic properties of a single polymer chain in the semidilute brush may be well-described by single-chain statistics such as the WLC model, at least in a highly stretched region, and that the adhesive force of the P4VP block on the AFM tip was strong enough to extend the graft chains up to about 90% of L_c. The distribution of L_c thus estimated was close to the chain length distribution of the PMMA block. This means that the length and length distribution of graft chains could be estimated by the AFM force analysis.

Introduction

Recently, the elastic properties of a single polymer chain end-grafted on a solid substrate surface have been investigated by atomic force microscopy (AFM).[1−7] In typical AFM experiments, an isolated graft chain is stretched by retracting the AFM tip on which a part of the graft chain is adsorbed (Figure 1a). This enables direct measurement of the elasticity of a single graft chain. The elastic properties of the graft chain in a polymer brush can be different from those of an isolated graft chain because of the interchain interactions in the brush. This is quite an interesting topic but has never been investigated before. This is presumably because of the difficulty of data interpretation: in a polymer brush, many chains would be adsorbed on the AFM tip at different, undefined sites along the chain so that the observed force profile would hardly be decomposed into the elastic responses of the individual chains.

Very recently, we succeeded in preparing the block copolymer brush comprised of low-polydispersity poly-(methyl methacrylate)-*b*-poly(4-vinylpyridine) (PMMA-*b*-P4VP) chains densely end-grafted on a silicon substrate by the surface-initiated atom transfer radical polymerization (ATRP) technique.[8] It was revealed that the short P4VP block at the free chain ends dramatically changes the surface properties of the brush without causing any significant change of the brush structure. In such a PMMA-*b*-P4VP block copolymer brush, the graft chains would be adsorbed on the hydrophilic surface of a probe sphere only at the P4VP block linked at the free chain end of PMMA, thus effectively simplifying the physical process, hence the interpretation of the force profile.

In this work, we have made an AFM study on the PMMA-*b*-P4VP block copolymer brush in toluene. Under this experimental condition, only the PMMA block of the brush would be swollen since toluene is a good solvent for PMMA and a nonsolvent for P4VP. The graft density of this bush (σ = 0.07 chains/nm^2) is high enough to form a "semidilute" polymer brush. This system has the mentioned advantage that the graft PMMA chain is stretched between the two chain ends (Figure 1b), which usually is not the case with conventional systems (Figure 1a). Experimental data will be analyzed by reference to the wormlike chain (WLC) model[9,10] to estimate the elasticity and the contour length of the PMMA graft chain.

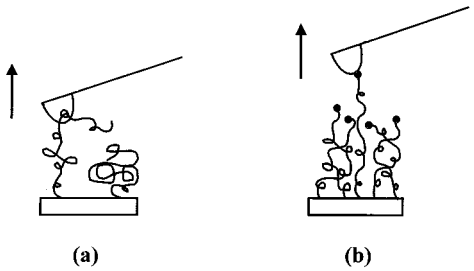

Figure 1. Schematic illustrations of single-chain stretching by the AFM tip: (a) conventional system; (b) this system.

Experimental Section

Preparation of the PMMA-*b*-P4VP Block Copolymer Brush. The PMMA-*b*-P4VP block copolymer brush was prepared by the reactivation of the dormant (potentially active) chain ends of the precursory PMMA brush in the presence of 4-vinylpyridine (4VP). The detailed procedures were described elsewhere.[8] In brief, the precursory PMMA brush[11] was subjected to the sequential polymerization of 4VP at 0 °C in a degassed dimethylformamide solution containing CuCl (6.4 mM), tris[2-(dimethylamino)ethyl]amine (6.4 mM), 4VP (2.3 M), and a free macroinitiator, Cl-terminated PMMA[13] (PMMA-Cl, 3.2 mM). The free macroinitiator PMMA-Cl was added in order to control the polymerization and to yield free polymers,

* To whom correspondence should be addressed. E-mail: fukuda@scl.kyoto-u.ac.jp.

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Table 1. Characteristics of the Block Copolymer Brush PMMA-*b*-P4VP

L_d[a] (nm)	5.3
σ[b] (chains/nm^2)	0.07
PMMA	
M_n[c]	56 600
M_w/M_n[c]	1.21
P4VP	
M_n[c]	2700

[a] Thickness in dry state. [b] The graft density σ was calculated from L_d,[a] $M_{n,PMMA}$, and the bulk density of the PMMA film (1.19 g/cm^3).[14] [c] Values for the free polymer produced in solution (see text).

which are useful as a measure of the molecular weight and molecular weight distribution of the graft chains.[8] After polymerization, the substrate was rinsed in a Soxhlet extractor with tetrahydrofuran (THF) for 12 h to remove physisorbed polymers and impurities. The characteristics of the PMMA-*b*-P4VP block copolymer brush studied are summarized in Table 1. In the table, the number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) are those for the free polymers produced in the solution, determined by a PMMA-calibrated gel permeation chromatographic analysis. There are reasons to believe that these values should well approximate those of the graft chains.[8,12]

AFM Measurement. Topographic imaging and force measurements were performed by an atomic force microscope (Seiko Instruments Inc., SPI3600) with a V-shaped cantilever (Olympus Optical CO., Ltd.), which had a spring constant of 0.16 N/m. A liquid cell was used for the measurement in toluene (Spectrograde, Dojindo Laboratories) at room temperature (about 25 °C). Interaction forces between the sample brush and the AFM tip in toluene (good solvent for PMMA) were measured as a function of the separation using a modified SPI3600 AFM apparatus, in which a piezo actuator of the one-dimensional layered type (Taiheiyo Cement, CO., PMF-2020 controlled by the piezo driver PM-1100) was installed, and its hysteresis behavior was corrected by simultaneously measuring its piezo current. Details of the force measurement were described elsewhere.[15] A number of force curves were collected with a scan rate of 0.5 Hz at different locations on the sample. Immediately prior to each force-curve measurement, the AFM tip was immersed in an aqueous solution (18% NH_3 solution: 30% H_2O_2 solution = 1:9 by volume) for 5 min to make the surface hydrophilic.

The raw AFM force curve (the cantilever deflection vs displacement curve) was converted into the force (F) vs separation (D') curve following the principle of Ducker et al.[16] The zero of D' is defined as the location of the so-called "constant compliance" plane beyond which the sample was no more compressible. The distance between the $D' = 0$ plane and the substrate surface is termed the "offset distance" D_o. We can determine D_o by the previously proposed "scratching method", in which we give a scratch to the sample to partly remove the polymer layer and make an AFM scanning across the scratch boundary to directly determine the layer thickness (at the constant compliance plane).[15] The true distance D between the surfaces of the substrate and the AFM tip may be given by

$$D = D' + D_o \tag{1}$$

The offset distance D_o generally depends not only on the sample but also on the AFM tip. We first employed an AFM tip with a silica probe (diameter, 10 μm), with which we measured D_o = 14 nm for our block copolymer brush. The *apparent* critical distance D_e' at which a repulsive force became detectable was 42 nm. Therefore, the critical distance from the substrate surface or the "equilibrium layer thickness" L_e is given by $L_e = D_e' + D_o = 56$ nm. In this study, we actually employed the V-shaped cantilever (without the silica probe), as mentioned above. The apparent critical distance D_e' of the same brush measured by this tip was 56 nm, which agrees with the above-mentioned value of L_e. This means that the D_o of the brush measured by this tip may be set equal to zero. Because of the sharpness of the tip and because of the relatively low graft density of the brush, the tip penetrated the brush, closely approaching the substrate surface. Thus, in this study, we can set $D' = D$. (The scratching method would be difficult to apply to systems with a very small or zero D_o, because they will give an unclear scratch boundary. This is the reason we made the mentioned analysis using the silica probe tip.)

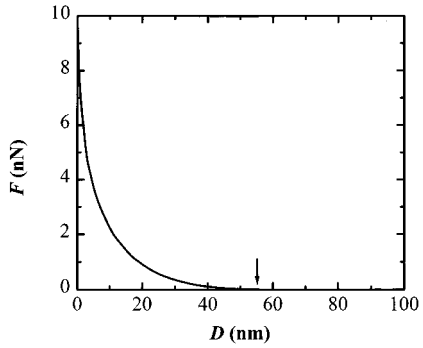

Figure 2. Advancing-mode force profile. The arrowhead indicates L_e.

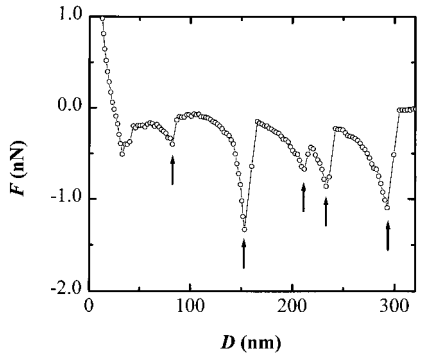

Figure 3. Retracting-mode force profile. The arrowheads indicate the attractive peaks, each arising from the detachment of a single chain from the AFM tip.

Results and Discussion

Force−Separation Profiles. Figure 2 shows the force (F) vs separation (D) relation (force profile) measured in the advancing mode. Repulsive forces arising from the steric interaction between the solvent-swollen brush and the AFM tip were observed. As already mentioned, the equilibrium thickness L_e of the solvent-swollen brush was determined to be 56 nm (Figure 2). This value of L_e corresponds to about 32% of the weight-average contour length $L_{c,w}$ (173 nm) of the PMMA chains forming this semidilute polymer brush (for the definition of L_c, see below).

Figure 3 shows a typical force profile measured in the retracting mode. Multiple attractive force peaks were observed in a single retracting cycle; the attractive force $-F$ (*minus F*) increased with increasing D and then suddenly dropped, giving a peak, and this response was repeated. This attractive force arises from the stretching of the graft chain between the substrate surface and the AFM tip. On the other hand, the precursor PMMA brush (with no P4VP block) gave almost the same repulsive force in the advancing mode but no attractive force in the retracting mode. This means that the P4VP block is so short that it has little effect on the brush structure studied by the advancing mode but it is

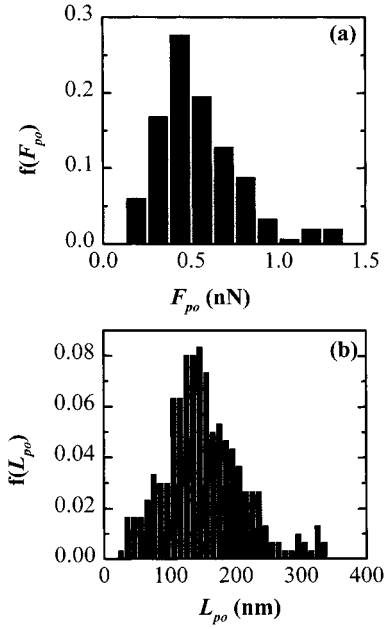

Figure 4. Probability distribution histgrams for (a) the pulling-off force F_{po} and (b) the pulling-off length L_{po}.

effectively adsorbed on the hydrophilic surface of the AFM tip. In other words, the AFM tip selectively picks up the graft chains at the P4VP block, not at the PMMA block. Each of the observed attractive peaks may be ascribed to the detachment of a single graft chain from the AFM tip.

Peak Analysis. The force and separation at each attractive peak-top will be termed the pulling-off force F_{po} and the pulling-off length L_{po}. (The pulling-off force has often been termed the "adsorption force".) Figure 4a shows the probability distribution histogram of F_{po}, which gives an average F_{po} of 0.55 nN with a standard deviation of 0.24 nN. This pulling-off force is larger than the previously reported values (for example, 0.2 nN for poly(methacrylic acid) and a Si_3N_4 AFM tip,[1] 0.25 nN for streptavidin and a biotin-covered tip[17]). However, it is much smaller than the force of 5−6 nN needed for breaking a C−C bond.[18]

Figure 4b gives the probability distribution histogram of L_{po}. The average and standard deviation of L_{po} were found to be 151 and 61 nm, respectively. It is interesting here to examine if the distribution of L_{po} should somehow reflect the distribution of the chain length. Using the relationship $L_{po} \approx 0.9L_c$, which will be established in the next section, we calculate the molecular weight M of the chain segment between the grafting and adsorbing points with

$$M = M_0 L_c / l_0 \qquad (2)$$

where L_c is the contour length (the full length in *all-trans* conformation), M_0 is the molecular weight of the monomer unit, and l_0 is the contour length per monomer unit ($l_0 = 0.25$ nm for PMMA). From the histogram in Figure 4b, M_n and M_w/M_n of the chain segment between the grafting and adsorbing points are estimated to be 64 000 and 1.16, respectively. Very interestingly, these values are close to those of the PMMA block (M_n = 56 600, $M_w/M_n = 1.21$).

Some comments may be necessary regarding this comparison of the two independent estimates of the chain length distribution of the surface-grafted polymer. One estimate is based on the assumption that the graft polymer is identical with the free (reference) polymer produced from the free initiator in the solution. The experimental evidence obtained so far suggests that these two polymers are nearly, but not exactly, the same. A difference in M_n on the order of 10% is expectable.[12c] The other estimate, which is based on the present AFM analysis, can also be in error, arising from two main sources: one is the relation $L_{po} \approx 0.9L_c$ used above. As will be discussed in the next section, the error included in this relation should be on the order of 10% at most. The other source of error is the possible nonrandomness in the picking-up (sampling) process of the graft chains by the AFM tip. If, for example, a longer chain is easier to be picked up than a shorter chain, the estimated distribution will be biased and give a larger M_n and a narrower distribution (a smaller M_w/M_n ratio) than they actually are. With all these possible errors in mind, the mentioned agreement of the two estimates of the chain length distribution of the graft polymer is indeed noteworthy, and it does suggest the validity of the AFM method.

Theoretical Analysis of the Attractive Peaks. Although discrete attractive peaks were observed in the force profile, the elastic response curves were more or less overlapped with each other. To avoid complexities, we analyze here only those response curves in which the attractive force reverts nearly to zero force (the baseline) after the detachment of the measured chain so that the effects of the subsequent response curves are negligible (cf. Figure 3). The wormlike chain (WLC), a wire model with a continuous curvature, is characterized by the persistence length q and the chain contour length L_c. The force F required to stretch a WLC in a solvent to an end-to-end length of D is given by

$$F = \frac{kT}{q}\left[\frac{D}{L_c} + \frac{1}{4(1 - D/L_c)^2} - \frac{1}{4}\right] \qquad (3)$$

where k is the Boltzmann constant and T is the absolute temperature. Figure 5a shows some experimental data fitted to the WLC model with q and L_c as adjustable parameters. The best-fit value of q was found to be nearly constant, about 0.3 nm, independent of L_c. All the response curves (with different L_c) were successfully scaled by D/L_c, giving a "master curve" as eq 3 predicts (see Figure 5b). The good agreement between the experimental data and the WLC model suggests that the model well-represents the elastic properties of a single polymer chain in the "brush" regime, as well as in the "dilute" regime.[1,5,6b] Figure 5b also revealed that the graft chains could be stretched up to about 90% of their L_c, i.e., $L_{po} \approx 0.9L_c$, with the pulling-off force F_{po} of about 0.6 nN. It should be reminded here that even though the analysis suggested by eq 3 applies only to single chains, its application to the multiple detachments observed in this case would be justified, since only those chains are observed where the force returns to the baseline, or almost to baseline, after each detachment. In addition, the possible effect of interactions with the other chains in the semidilute equilibrium layer should be minor, since the observed chains are stretched far out from the (relatively thin) equilibrium layer.

The mentioned analysis based on the WLC model allows us to estimate the three parameters, which were as follows: $q = 0.3$ nm, $F_{po} = 0.6$ nN, and $L_{po} = 0.9L_c$. Needless to say, these estimates are dependent on the

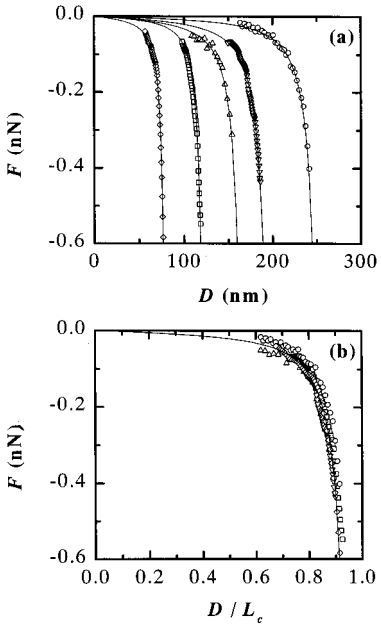

Figure 5. (a) Experimental force curves for stretching of the single PMMA graft chains (symbols) and their WLC-fitted curves (solid curves). (b) Master curve for all the experimental data (symbols) and the WLC fit (solid curve).

model and the accuracy of the experimental set up. We expect that the spring constant of the AFM cantilever used in our experiments can be in considerable error (at least several tens of percent), which directly affects the values of q and F_{po}. The value of q is also strongly model dependent, and we are not sure at all that a WLC chain is the best model to represent the elastic properties of PMMA quantitatively. For these reasons, we should not put too much importance on the estimated values of q and F_{po}. On the other hand, we expect that the value of L_{po}/L_c is less seriously dependent on absolute force values and the model. For example, if F_{po} is assumed to be 0.3 nN (half of the above estimate), L_{po}/L_c will be estimated to be about 0.85, instead of 0.9 for $F_{po} = 0.6$ nN (cf. Figure 5b). In the same vein, if, for example, the freely jointed chain (FJC) is used instead of WLC, L_{po}/L_c will be estimated to be somewhat larger than 0.9, since a FJC is more easily stretched than the WLC with the same q.[19] These considerations suggest that we were able to determine the L_{po}/L_c ratio to be in a rather narrow range of about 0.9.

Conclusions

The introduction of a short P4VP block at the free chain ends of a PMMA brush made it possible to selectively pick up the chain ends and stretch the graft chains by an AFM tip. Upon retracting the AFM tip, discrete multiple attraction peaks were observed, each of which was attributed to the detachment of a single graft chain from the AFM tip. Each elastic response curve could be well-fitted to the WLC model, giving an estimate of the contour length L_c of the related single chain. These analyses revealed the following: (i) the elastic properties of a single polymer chain in the semidilute brush may be well-described by single-chain statistics such as the WLC model at least in a highly stretched region; (ii) the adhesive force of the P4VP block on the AFM tip was strong enough to extend the graft chain up to about 90% of its contour length L_c; (iii) the distribution of L_c thus estimated was remarkably close to the chain length distribution of the PMMA block.

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