Macromolecules

Volume 36, Number 11 June 3, 2003

Communications to the Editor

Desorption Force per Polystyrene Segment in Water

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Received January 23, 2003
Revised Manuscript Received April 15, 2003

Polymers at interfaces are a traditional but challenging topic in polymer science and now especially in supramolecular science. Related studies have mainly focused on two aspects: energy and conformation. The spontaneous adsorption of a polymer chain onto a solid−liquid interface in solution minimizes its free energy. In general, a polymer chain adsorbed on a substrate can adopt the conformation of the "train", "loop", and "tail", depending on the nature of polymer and substrate.[1] Such chain conformations on a surface have been extensively studied by various spectroscopic method, including nuclear magnetic resonance,[2] infrared,[3] and electron spin resonance spectroscopy.[4] Entropy or enthalpy or both can drive the adsorption process. Therefore, it is important to know the interaction strength per polymer segment adsorbed on a substrate. However, a direct measurement of the interaction energy between a given polymer chain and a substrate is rather difficult.[5] This is why only a few experimental studies have been reported so far in this direction.[6−8]

Recently, single molecule force spectroscopy (SMFS) developed on the basis of atomic force microscopy (AFM) has become a versatile platform for studying inter- and intramacromolecular interactions with an extremely high force sensitivity.[9] Using SMFS, a number of interesting topics, such as protein unfolding,[10] DNA deformation and unzipping,[11] force-induced conformational transition,[12] host−guest interaction,[13] and single chain elasticity,[14] have been investigated. In particular, Samorì[15] proposed a new SMFS method to detect the chain conformation on a surface. Moreover, the adsorption/desorption energy of a single polymer chain on a surface can also be obtained. It is helpful to note that, for a homopolymer or statistically random copolymer chain, the adsorption normally results in a mixture of trains, loops, and tails on a surface.[16] Therefore, one has no control over the number of monomer units adsorbed on each site. We normally measure only the average interaction strength per chain, not per monomer unit, adsorbed on the substrate. To solve this problem, we prepared a segmented copolymer in which short hydrophobic polystyrene (PS) segments were more uniformly inserted into a thermally sensitive linear poly(*N*-isopropylacrylamide) (PNIPAM) chain backbone by micelle copolymerization. Details of the synthesis and characterization can be found elsewhere.[17] The structure and composition of such a copolymer chain are schematically shown in Figure 1a. Taking one PNIPAM segment together with its adjacent PS segment as a "repeat unit", which is ∼100−130 nm in length,[18] each copolymer chain, on average, contains ∼90 such "repeat units". It should be noted that micelle copolymerization determines that the distance between two neighboring PS segments obeys a Gaussian distribution. The schematic of the hydrophobic adsorption of these short PS segments (∼2 nm[18]) onto a PS substrate in water is shown in Figure 1b. An aqueous solution of the copolymer (5 mg/L) was stored at 20 °C for 1 week to ensure a complete dissolution.

The flat PS substrate was prepared from a sheet extruder, which was sufficiently smooth for SMFS. The PS segments are so short that the surface can be considered very smooth; i.e., each PS segment was laid flat on the substrate. Before the adsorption, the PS substrate was thoroughly rinsed with ethanol (99.5%)

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10.1021/ma034090e CCC: $25.00
Published on Web 05/02/2003

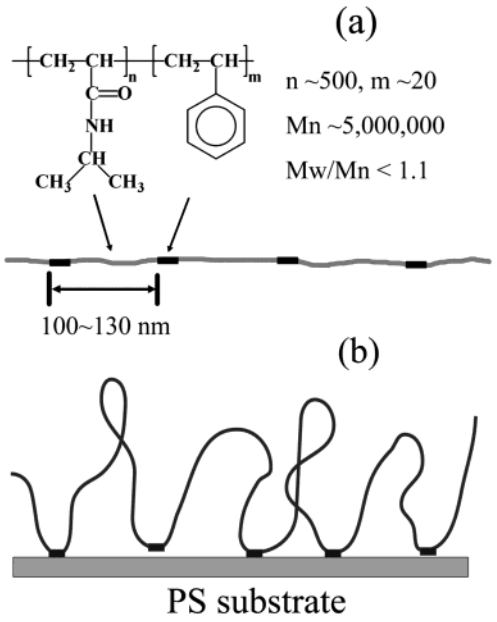

Figure 1. (a) Schematic of a linear segmented poly(*N*-isopropylacrylamide-*seg*-styrene) coplymer chain prepared by micelle copolymerization, in which short PS segments are relatively evenly distributed on the chain backbone. (b) Schematic of the adsorption of a linear PNIPAM-*seg*-PS chain on a hydrophobic PS substrate in water.

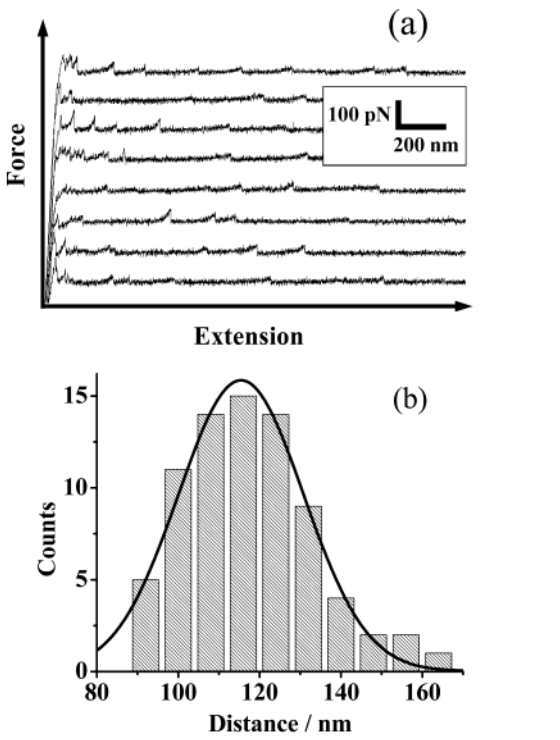

Figure 2. (a) Measured force curves of linear segmented poly(*N*-isopropylacrylamide-*seg*-styrene) chains adsorbed on a hydrophobic PS substrate in water. (b) Statistics of the distance between two adjacent peaks in the measured force curves.

and purified water (>18 MΩ cm) and then confirmed as a blank sample by SMFS. (SMFS did not detect an obvious force signal during over 1000 cycles of AFM tip's approach and retraction.) Then PNIPAM-*seg*-PS aqueous solution (~0.2 mL) was deposited on the PS substrate and left for approximately 12 h to form a thin layer. Afterward, the sample was rinsed with purified water for 1 min to remove loosely adsorbed PNIPAM-*seg*-PS before being measured. A homemade SMFS with a silicon nitride cantilever (Park, Sunnyvale, CA) was used.[19] The calibration of each tip using a standard sample has been described before.[14b] The spring constants of these cantilevers were in the range 0.010−0.012 N/m.

By moving the piezo tube, we could bring the sample into contact with the AFM tip so that some polymer chains were physisorbed onto the tip, resulting in a number of "bridges". As the distance between the tip and the substrate increased, the chains were stretched and the elastic force deflected the cantilever. A recorded deflection−piezo path curve was converted into a force−extension curve, i.e., the force curve. It has been shown that the adhesion force between the tip and the adsorbed chain can be up to a few nanonewtons in magnitude.[19,20] Therefore, using SMFS, we can measure the weak interaction force between a single polymer chain and the substrate. The stretching velocity used was in the range 520−4600 nm/s. The instrumentation and theory of SMFS have been detailed elsewhere.[9,19]

Prior to the force measurement, a drop of purified water, acting as a buffer, was injected between the substrate and the cantilever holder, whereupon both the substrate and the cantilever were immersed in water. The force measurements were performed at ~22 °C, at which temperature long PNIPAM segments are hydrophilic and soluble in water with a random coil conformation. Dynamic laser light scattering confirms that PNIPAM-*seg*-PS does not form micelle in this case.[21] It is reasonable to expect that the adsorption of insoluble short hydrophobic PS segments onto the PS substrate resulted in many PNIPAM "loops". Figure 2a shows that the force curves exhibit a similar characteristic, namely, a saw-tooth pattern. To find why such a pattern exists and how it is related to the chain structure, we analyzed statistically the distance between each two adjacent peaks in the force curves, as shown in Figure 2b. The Gaussian fitting of the histogram led to an average distance of ~114 nm. This value is very similar to the average length of the "repeat unit" (one long PNIPAM segment plus one short PS segment) in the copolymer chain. This coincidence is rationalized by the micellar polymerization.[17] These results suggest that the copolymer chain does form loops with a similar size on the PS substrate. Therefore, the saw-tooth pattern corresponds to the detachment of the adsorbed segments in a single chain from the substrate.

In contrast, the force curves obtained on a quartz substrate modified with hydroxyl groups (Figure 3a)[22] are very different from those obtained on a PS substrate. Figure 3b shows that the force curves corresponding to different contour lengths superimpose well after normalization, indicating a single chain stretching.[23,24] The PNIPAM-*seg*-PS copolymer chain on a quartz substrate shows a force curve similar to a PNIPAM homopolymer chain on a glass substrate,[23] which is predictable since short hydrophobic PS segments cannot adsorb onto the hydrophilic quartz substrate and only PNIPAM segments contribute to the resulting force curve. The rupture force on the quartz substrate indicates that the adhesion force between the copolymer chain (or PNIPAM segments) and the AFM tip is stronger than 200 pN, much stronger than the rupture force on the PS substrate. This finding confirms that the weak rupture force obtained on the PS substrate corresponds to the desorption of short PS segments from the substrate.

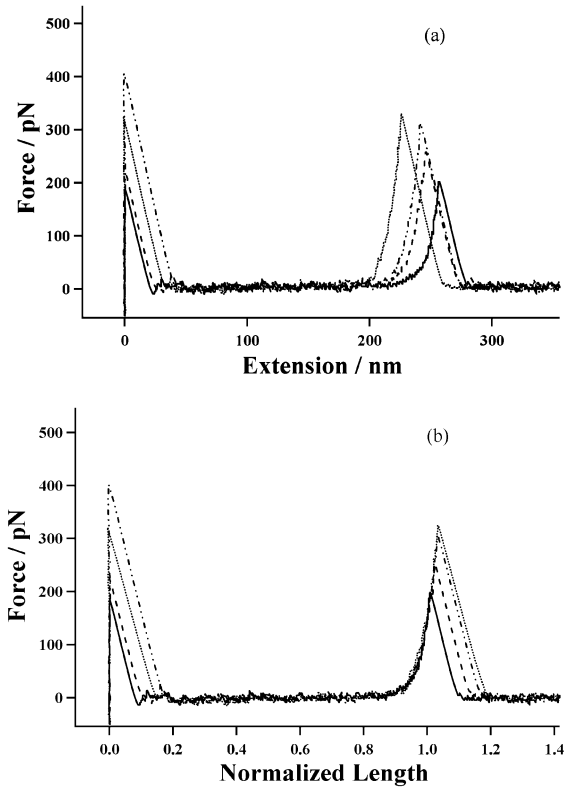

Figure 3. (a) Measured force curves of linear segmented poly(*N*-isopropylacrylamide-*seg*-styrene) chains adsorbed on hydrophilic quartz substrate. (b) Normalized force curves on the basis of (a).

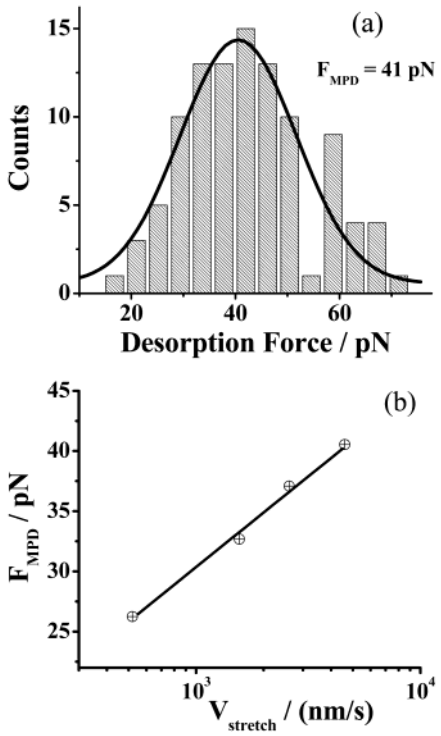

Figure 4. (a) Distribution of the measured desorption force for linear segmented poly(*N*-isopropylacrylamide-*seg*-styrene) copolymer chains adsorbed on hydrophobic PS substrate, where the stretching velocity is kept at 4600 nm/s. (b) Stretching velocity ($V_{stretch}$) dependence of the most probable desorption force (F_{MPD}).

Figure 4a shows that for a given stretching velocity ($V_{stretch}$) the desorption force essentially follows a Gaussian distribution, and the most probable desorption force (F_{MPD}) is ∼41 pN. Such a distribution varies with the stretching velocity. Figure 4b shows that F_{MPD} increases with the stretching velocity. The linear dependence of F_{MPD} on log($V_{stretch}$) has been predicted by Evans,[25] indicating that the adsorption and desorption of the PS segments on the PS substrate is a dynamic process. In the stretching velocity range of 520−4600 nm/s, the escape of short PS segments with an average length of ∼2 nm from the PS substrate implies that the desorption lifetime is in the range ∼0.4−4 ms. Evans[25] showed that noncovalent binding of a chain on a substrate could eventually undergo the desorption even without any external force. The presence of an external pulling force can only shorten the desorption lifetime. Therefore, considering the experimental time range, we estimate that the innate desorption lifetime should be much longer than ∼4 ms, corresponding to the lowest stretching velocity used. Considering the range (26−41 pN) of F_{MPD} (Figure 4b) and the average length (∼2 nm) of short PS segments, we can estimate that the average desorption work of each PS segment from the PS substrate is in the range 30−49 kJ/mol,[26] depending on the stretching velocity. In other words, the desorption energy per unit area between the PS segment and the PS substrate is in the range 0.017−0.026 J/m^2,[27] consistent with Pashley's results, which was obtained on much larger surfaces.[27] The measured desorption force we measured per PS segment using SMFS therefore seems reasonable.

After comparing the adhesion energies between the measured and calculated results based upon van der Waals theory, Pashley et al.[28] found that the measured values were much higher than the calculated values as long as the distance between two hydrophobic surfaces is less than 8 nm. In other words, the van der Waals interaction contributes little to the adhesion energy over a short distance. We estimate that the measurable distance between the PS segment and the PS substrate in SMFS is less than 1 nm.[28] Therefore, the adsorption of the PS segments onto the PS substrate in water is predominantly driven by short-range hydrophobic interaction. Pashley et al. also showed that the adhesion energy between two hydrophobic surfaces is exponentially dependent on the distance between them. Different from two approaching flat surfaces,[28] the distance between the PS segment and substrate in the present experiment is not a constant since the adsorption and desorption is a dynamic process, which explains the force distribution for a given stretching velocity in Figure 4a.

In summary, the adsorption of short hydrophobic polystyrene segments of a specially prepared long linear amphiphilic poly(*N*-isopropylacrylamide-*seg*-styrene) (PNIPAM-*seg*-PS) copolymer chain onto a polystyrene (PS) surface can lead to the formation of many PNIPAM loops whose sizes follow a Gaussian distribution. Using single molecule force spectroscopy (SMFS), we have successfully measured, for the first time, the distribution of the desorption force per PS segment adsorbed on the PS substrate in water. The linear dependence of the most probable desorption force on the logarithm of the stretching velocity experimentally reveals that the adsorption and desorption of the PS segments on the PS substrate is a dynamic process. Since we know each PS segment contains 20 monomer units on average, we estimate that the desorption force per PS monomer unit

from the PS substrate in water is in the range 1.3−2.1 pN, depending on the imposed stretching velocity. Compared with previous achievements using different methods,[2−8] this study provides a more direct determination due to its single chain manipulation.

Acknowledgment. This study was supported by the Major State Basic Research Development Program (Grant G2000078102), the Ministry of Science and Technology and Natural Science Foundation of China. We thank Prof. Hermann E. Gaub for his help in establishing the SMFS setup and Dr. Guangzhao Zhang for synthesizing the copolymer used in this study. Chi Wu thanks the Croucher Foundation for awarding him a Senior Research Fellowship. We also gratefully acknowledge Dr. Barbara Whitesides from Harvard University for carefully polishing the English of this paper.

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MA034090E