Direct Measurements of Stretching Force-Chain Ends Elongation Relationships of a Single Polystyrene Chain in Dilute Solution

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Mechanical stretching characteristics of a single polystyrene chain in a dilute solution was investigated with atomic force microscope. An entropic elasticity expressed by the extended Langevin function was observed in a force range below 200 pN and an extension range below 60 nm.

It is well known that when both the ends of a flexible polymer chain are pulled, it behaves like a spring in theory due to entropy reduction.[1,2] Recently, experimental studies have been performed on stretching a single DNA molecule.[3-6] Stretching measurements for a single protein or dextran have also been carried out with atomic force microscope (AFM).[7,8] In this study, mechanical stretching behavior of a single chain of polystyrene (PS) was investigated in a dilute solution with AFM.[9]

PS used in this study was synthesized by a living anion polymerization. A carboxyl group, which was expected to form a covalent bond with a hydroxyl group by dehydration reaction, was attached to each chain end by terminating the polymerization reaction with CO_2. The surfaces of silicon nitride cantilevers with spring constant of 0.01 Nm^{-1} and silicon wafer substrate were treated with H_2O_2 to form hydroxyl groups. AFM (Nanoscope III, Digital Instruments) was used for measuring a force-extension-curve, that is, the relationship between magnitude of deflection of the cantilever corresponding to force and displacement of the cantilever from the substrate surface. The tip was moved vertically downward and upward with respect to the substrate(silicon wafer) in a 10^{-5} M PS solution at 293 K. Toluene was used as good solvent for PS at measured temperature. Measurement of a force-extension curve was repeated at 0.2 Hz more than 1,000 times. The tip-substrate distance was corrected by the magnitude of deflection of the cantilevers.

The gel permeation chromatography measurements showed that number-average molecular weight, Mn of the synthesized PS was 27,000, then the average degree of polymerization was 260. The polydispersity index, Mw/Mn was 1.81. The average radius of gyration of random coil in an unperturbed was about 4.5 nm using the characteristic ratio, C=10,[10] though the PS random coil should be a little more extended in the toluene solution because of a good solvent. In the case of the solution of 10^{-5} M, the average distance between centers of gravity for the random coils in the solution was about 12 times as large as the estimated radius of gyration.

Figure 1 shows the typical examples of force-extension-curves. In the almost all cases, no considerable attractive force was detected as shown in Figure 1(a). Some attractive force corresponding to stretching response of polymer molecules was measured as shown in Figure 1(b),(c), with the occurrence frequency of around 15%. The magnitude of ultimate stretching strengths, σ_{max} calculated from the maximum deflection and the spring constant of cantilever, ranged 10~50 pN. The stretching responses with σ_{max} ranging 200~250 pN were very rarely observed with the occurrence frequency of 0.5%. Those responses could be understood to arise from bridging links between both surfaces of tip and substrate by PS chains because no response was found in pure solvent. When a single breakdown as shown in Figure 1(c) was observed, it is statistically reasonable to consider that a single PS chain was stretched between the substrate and tip surfaces. The small bump just above the zero distance as shown in Figure 1(c) might be due to a direct adhesion of tip surface onto the substrate surface because the similar behavior was sometimes observed in solvent. If plural chains were bridged at once between the tip and substrate surfaces, several breakdowns should be observed as shown in Figure 1 (b).

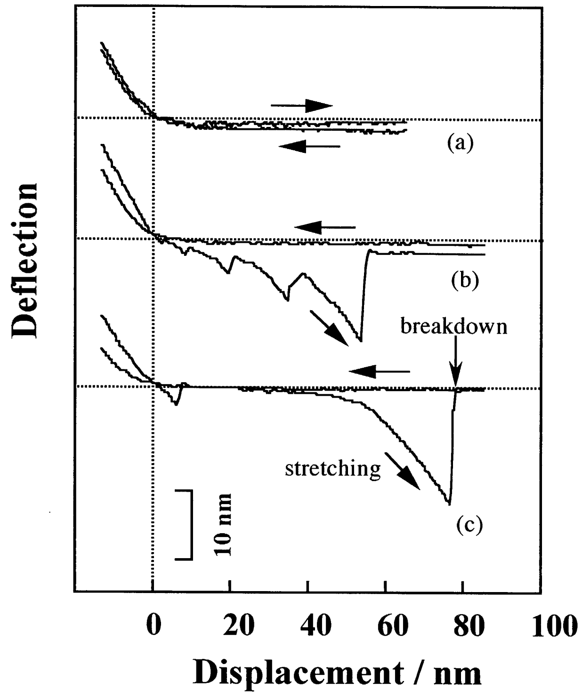

Figure 1. Plots of the magnitude of deflection of the cantilever against the displacement of cantilever with respect to the substrate surface.

The σ_{max} ranging 200~250 pN was obtained only in the case that both the ends of a PS chain were chemically modified. The magnitude of force to dissociate a covalent bond can be calculated on the basis of the Morse potential. Since the binding energy of C-C covalent bond is 360 kJ mol^{-1},[11] the magnitude of force at break for the C-C covalent bond can be roughly calculated to be 5-6 nN based on the Morse potential. Also, the energy to separate the van der Waals force is around 1 kJ mol^{-1}. Using the

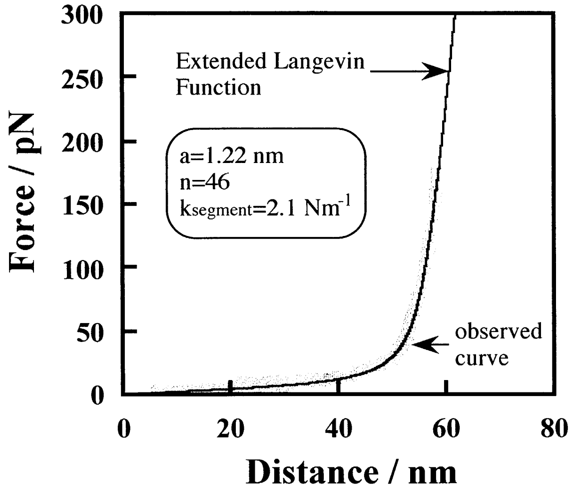

Figure 2. Experimental stretching force-distance curve(bold line) and fittable calculated curve (solid line) based on extended Langevin function.

order of typical Harmaker constant, 10^{-9} J,[11] the magnitude of van der Waals force between atoms in PS and substrate should be under several 10 pN. Since the binding energy of hydrogen bonding is known to range from 10 to 40 kJ mol^{-1},[12] the magnitude of force to break a single hydrogen bond would be intermediate between covalent bond and van der Waals force. Therefore, the experimental values for $\sigma_{\max}$ ranging 10~50 pN might correspond to the van der Waals force between a PS chain and substrate or tip surface. On the other hand, the magnitude of $\sigma_{\max}$ ranging 200~250 pN might be assigned to the hydrogen bond between -COOH group at the end of chain molecule and -OH one on the substrate or tip surface, although there is much left to study to identify the type of bond.

The bold line in Figure 2 shows the experimental curve of the stretching force against the tip-substrate distance which was corrected for the data in Figure 1(c). A monotonously increasing curve was obtained for the force-distance plot before the breakdown. Based on the Langevin function, it is possible to compute the average chain-end separation for a chain subjected to a stretching force applied to the chain ends for an ideal freely jointed chain. However, the experimental force-distance curve did not fit to the calculation based on the Langevin function. The curve fitting was tried on the basis of the extended Langevin function which was formulated based on an entropy spring being composed of elastic segments.[6,8] The extended Langevin function is expressed by equation (1).

$$r(f) = \left[\coth\left(\frac{af}{k_B T}\right) - \frac{k_B T}{af}\right]\left(na + \frac{nf}{k_{segment}}\right) \qquad (1)$$

where r, f, a, k_B, T, n, and $k_{segment}$ are the distance between end-to-end of a chain, the stretching force applied to the chain ends, the statistical segment length, the Boltzmann's constant, temperature, the number of segment, and the elastic constant of the segment, respectively. If the Kuhn segment length for PS chain, about 0.68 nm, was used as the a, the experimental force-distance curve could not be fit by equation (1) by adjusting with any values of other parameters. When a=1.22 nm (about 8 times as long as the C-C bond length), n=46, and $k_{segment}$=2.1 Nm^{-1} were used, the calculated force-distance curve agreed well with the experimental one as shown in Figure 2. However, the magnitude of $k_{segment}$ mentioned above was extremely small compared to the spring constant for the steric structural change of a PS backbone chain, for example, the change in the C-C-C bond angle, for which the spring constant is about 120 Nm^{-1}. The speculated reason is discussed below.

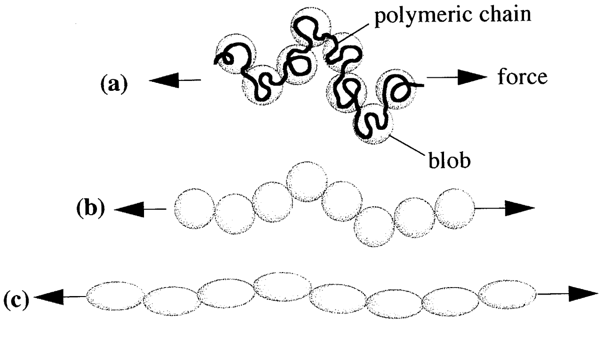

Figure 3. Schematic illustration of possible conformation model of flexible chain molecule in good solvent and its stretching behavior.

It is presumed that a flexible polymeric chain forms a random coil with chained blobs consisting of small random coils in a good solvent as shown in Figure 3(a).[2] A PS chain in a toluene solution could be represented by a model that the blobs consisting of several monomer units are linked together in a row. The stretching force might make the sequence of blobs varied from random to nearly straight as schematically illustrated in Figure 3(b). Then, the shape of each blob might deform from spherical to ellipsoidal with further stretching as shown in Figure 3(c). The deformation process of a PS chain indicates that the anomalously small $k_{segment}$ used for the curve fitting may be attributed to the elasticity of the blob deformation.

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