Communication

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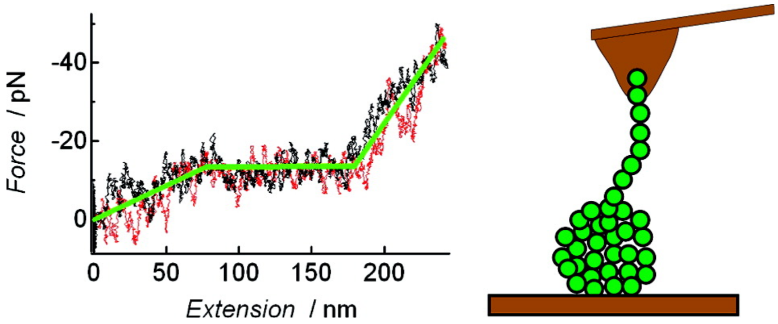

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Force-Induced Globule-Coil Transition in Single Polystyrene Chains in Water

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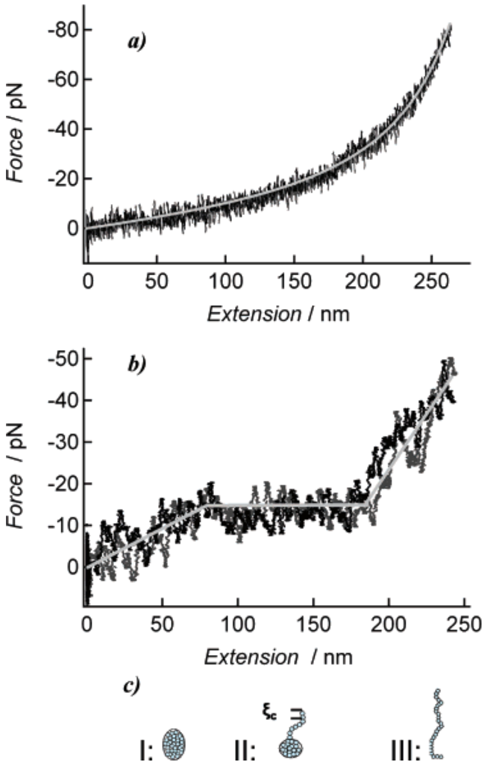

Figure 1. Black curve shows extension (pulling) of single molecule and gray curve shows retraction (relaxation). (*a*) Reversible nonlinear extend−retract cycle of an individual polystyrene (PS) chain exhibiting entropic chain elasticity in toluene (good solvent condition). The gray solid line is the WLC fit. (b) Reversible extend−retract cycle of an individual, collapsed PS chain in water obtained at 150 nm/s pulling speed exhibiting a plateau force at ∼13 pN. (c) Drawings at bottom illustrate the chain configurations predicted by the Halperin (11) and Cooke (12) models of the extension of a single polymer chain in poor solvent.

The collapse of a hydrophobic polymer in water is a basic model for many-body hydrophobic interactions that gives insights into forces that determine surfactant and synthetic polymer nanostructures, as well as protein folding.[1−5] Recently, the collapse of a single hydrophobic chain in water was studied using a computer simulation that revealed the evaporation of water in the vicinity of the chain leads to the nucleation of hydrophobic units which is the driving force for collapse; the transition was observed to be like that of a first-order phase transition.[6] Force induced conformational transitions of polyelectrolytes,[7] individual protein molecules,[8−10] polysaccharides,[11] and some other biopolymers have provided fundamental information on their internal structure. Hydrophobic collapse is seen as a primary driving force in macromolecule self-assembly, but such a collapse has not been isolated directly on the single molecule level by experimental measurements, for either synthetic or natural polymer chains. Force-induced stretching of single chains that are collapsed in moderately poor solvents was first studied theoretically more than a decade ago by Halperin et al.[12] and more recently in strongly poor solvent conditions by Cooke et al.[13]

This paper describes the force-induced mechanics of individual polystyrene (PS130000) chains in strongly poor, moderately poor, and good solvent conditions. The homopolymer films were spun-cast onto precleaned silicon substrates from dilute toluene solutions and studied under different solvents. The "recycling" or "fly fishing" method[14] of single molecule force spectroscopy was used, which involves gently catching and then repeatedly stretching and relaxing individual chains without bringing the tip into compressive contact with the surface, thereby avoiding extension profiles that result from the interaction with several molecules.[15] (see Supporting Information)

Figure 1a shows that PS exhibited a wormlike chain (WLC) deformation in toluene (good solvent) giving a persistence length value of (0.25 ± 0.05) nm consistent with literature.[16] Figure 1b shows a typical extend−retract cycle of a single PS chain measured in water at a pulling speed of 150 nm/s. A box smoothing window was applied to the data shown (depending on the pulling speed 11−51 points were averaged). The profile is qualitatively different from that seen in toluene. In water, in regime I the force rises linearly up to ∼13 pN. In regime II, with further extension a plateau force is observed at ∼13 pN. The plateau force was determined by the average over the linearly fitted plateau region. In regime III, the force rises again linearly. The fact that the magnitude of plateau force does not vary on changing the tip surface (gold coated and silicon nitride) and substrate (silicon, gold, and mica) indicates that chain desorption from a surface of the tip or substrate can be excluded (see Supporting Information). The reproducibility of the force profile upon constant recycling of the extension of a single molecule indicates that chain sliding across the surface does not play a significant role (see Supporting Information).

These three regimes of deformational behavior were approximately predicted by first Halperin et al.[12] and later Cooke et al.,[13] (see Figure 1c, bottom). In Halperin's model, the origin of the linear restoring force in Regime I is due to deformation of a collapsed, spherical globule to an ellipsoid, hence creating an excess area that leads to an excess surface energy. Regime II is associated with a conformational transition involving the coexistence of the globule and a stretched chain of polymer or polymer globules. Finally for strong stretching, the force-extension behavior of a Gaussian chain is recovered (region III).

The plateau force was observed to be loading rate dependent (see Supporting Information). At pulling speeds below ∼150 nm/s, the extend−retract profiles were experimentally indistinguishable (Figure 1b). Hence at these rates, the extension process occurs

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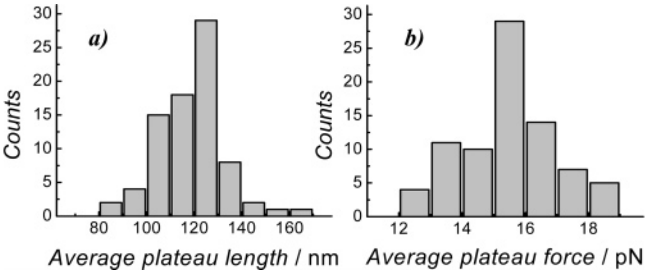

Figure 2. Statistical analysis of extend−retract curves ($n = 80$) obtained at 150 nm/s. (a) Histogram of average plateau length giving a mean value of (118 ± 14) nm. (b) Histogram of average plateau force giving a mean value of (15 ± 1.4) pN.

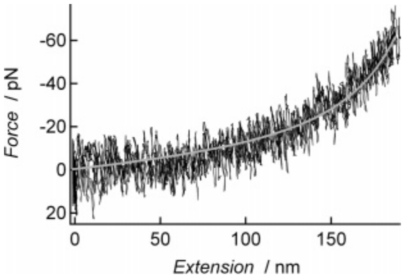

Figure 3. Reversible nonlinear extend−retract cycle of an individual polystyrene (PS) chain obtained at 500 nm/s pulling speed in 6 M GdnHCL aqueous solution. The gray solid line is the WLC fit giving a value of (0.20 ± 0.03) nm.

slowly enough for the chain to explore freely its configurational degrees of freedom, other than end-to-end distance, and the area underneath the plateau reflects the free-energy changes associated with the globule−coil transition. To estimate the free-energy change, a statistical analysis on the plateau force and plateau length was carried out. Figure 2 panels a and b show the histogram of average plateau length and average plateau force on measurements ($n = 80$) carried out at 150 nm/s giving a mean plateau length of (118 ± 14) nm and a mean plateau force of (15 ± 1.4) pN. Thus we obtain a mean free energy of $\Delta G = 1066 \pm 125$ kJ mol^{-1} over ∼120 nm of extension. Assuming the tension has extended the chain so that each monomer is fully exposed to solvent (an approximation), these ∼450 monomers (contour length contribution of 0.25 nm/monomer) exhibit a per monomer solvent exposure cost of ca. 2 kJ/mol.

Halperin predicted the three regime, force-extension curve for a polymer being stretched in a moderately poor solvent. Since water is a bad solvent for PS, we studied the force-extension behavior of PS in propanol (moderately poor solvent). The extend−retract cycle showed a nonlinear behavior similar to that observed in Figure 1a). This may suggest that the plateau force may be due to hydrophobic interactions. However, propanol has a lower surface tension as compared to water on PS surface, and according to Halperin's model the plateau force depends on the interfacial energy. To test whether the globule-coil transition could be independent of interfacial energy, as would be true if hydrophobic interactions played a role, measurements in aqueous solution in the presence of guanidine hydrochloride (GdnHCL) were carried out.

Extensive studies[17−19] have shown that salts such as urea and GdnHCl disrupt hydrophobic interactions. The surface tension of 6 M GdnHCl is slightly higher than that of pure water, and the interfacial energies of PS with water and GdnHCl obtained by contact-angle measurements on PS spin-coated samples were both 45 ± 1 mN/m. Single molecule extension measurements on PS were carried out in 6 M GdnHCL aqueous solution. The plateau profiles seen in pure water disappeared in 6 M GdnHCl, as shown in Figure 3. Occasionally, the extend−retract cycle of single PS chains measured at 500 nm/s showed a short (<15 nm) low plateau exhibiting a force of ∼15 pN (see Supporting Information). Kosmotropic salts such as sodium chloride (NaCl) are known to enhance hydrophobic interactions.[20] Measurements were carried out in 1 M NaCl solution and an increase in the plateau force to ∼27 pN was observed at a pulling speed of 150 nm/s (see Supporting Information).

In summary, a constant force associated with a globule−coil transition of single polystyrene chains was observed in pure water but not in moderately poor solvent or 6 M GdnHCl solution exhibiting approximately the same PS-liquid interfacial tension, whereas in the presence of 1 M NaCl the magnitude of plateau force increases. These observations suggest that the constant force measured in pure water may have a dominant contribution from hydrophobic interactions.

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Supporting Information Available: Force-extension curves, "re-cycling" curves, and details on the experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

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