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Single-Chain Elasticity of Poly(ferrocenyldimethylsilane) and Poly(ferrocenylmethylphenylsilane)

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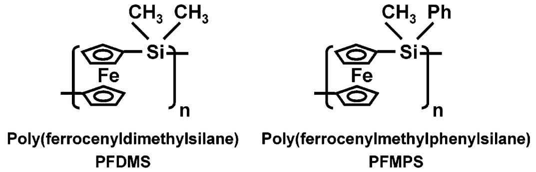
ABSTRACT: AFM-based single-molecule force spectroscopy (SMFS) is a powerful tool for the investigation of the elastic properties of a single polymer. Two typical organometallic polymers bearing ferrocene (Fc) groups in the backbone, poly(ferrocenyldimethylsilane) and poly(ferrocenylmethylphenylsilane), were investigated by SMFS to reveal their single-chain mechanical properties in normal and oxidized forms. We have found that the two polymers show similar elasticity in normal forms, though bearing different side groups. However, they exhibit different enthalpic elasticity after oxidation probably because of steric effects. Moreover, all experiments confirm that the single-chain elongation of poly(ferrocenyldimethylsilane) or poly(ferrocenylmethylphenylsilane) is reversible.

Introduction

The appearance of atomic force microscopy (AFM) has extended our ability to explore the small world. It has been shown that AFM-based single-molecule force spectroscopy (SMFS) is powerful not only in understanding the elastic properties of single polymer strands but also in exploiting the conformational changes of single polymers, bringing us with valuable fingerprint information on single polymers, which is not accessible by conventional methods.[1] The new information provides new insights into the mechanical properties of polymers at the molecular level, such as the force−extension relationship of random coils,[2] the chair-to-boat conformational transition of individual glucopyronose rings,[3] the single-molecule photomechanical cycle of azopolymers,[4] splitting or unwinding of helical structures,[5] the detachment of single polymer chains from the substrate,[6] and the polydispersity index.[7] In addition, combining SMFS with specially designed systems, researchers have measured directly host−guest interactions,[8] hydrophobic interaction,[9] and even the strength of single covalent bonds,[10] and so on.

Nowadays, metal-containing polymers are of growing importance for introducing redox, magnetic, optical, or catalytic properties into polymer materials. And the introduction of different type of intermolecular interactions can even lead to create supramolecular materials.[11] Following the pioneer work of Manners,[12] we have prepared poly(ferrocenyldimethylsilane) (PFDMS) and poly(ferrocenylmethylphenylsilane) (PFMPS) by ring-opening polymerization, as shown in Scheme 1.[13] The two polymers bear the same main-chain structure but different Si-substituted groups: two methyl for PFDMS and one methyl plus one phenyl for PFMPS. In addition, the ferrocene (Fc) groups bearing in the polyferrocenylsilane (PFS) can be oxidized easily to the corresponding cation, ferrocenium.[12,14,15] Using SMFS, in this paper we attempt to investigate comparatively force spectroscopy on these two PFS. Our research is aimed to reveal the effect of side groups on single-chain elasticity of such metal-containing polymers and to see whether there is an elastic difference before and after oxidation.

Scheme 1. Chemical Structures of Poly(ferrocenyldimethylsilane) (PFDMS) and Poly(ferrocenylmethylphenylsilane) (PFMPS)



Experimental Section

The synthesis of PFDMS and PFMPS samples has been reported previously.[13] The weight-average molecular weight, M_w, of PFDMS is 6.92×10^5 g/mol, and its polydispersity index, M_w/M_n, is 1.3. The M_w of PFMPS is 1.10×10^5 g/mol, and its polydispersity index is 2.3. The molecular weights are measured by GPC using polystyrene as standard.

The two polymers were dissolved in tetrahydrofuran (THF) or dichloromethane (CH_2Cl_2) to a concentration of approximately 3.4×10^{-6} g/mL. The CH_2Cl_2 solutions of the two polymers were oxidized using excessive anhydrous $FeCl_3$. The reaction occurred spontaneously as indicated by the rapid color changes from clear yellow to green and then blue.[12,14,15] Approximately 0.1 mL of the PFDMS−THF solution was dropped onto a cleaned quartz substrate[16] and incubated, at room temperature, for 10 min. The excess liquid was removed from the substrate, and the substrate with polymer was ready for SMFS measurement. The sample of PFMPS for SMFS experiment was prepared in the same way. Because of the fast volatilization of CH_2Cl_2, we immersed a quartz substrate in CH_2Cl_2 solution of oxidized PFDMS (o-PFDMS) or oxidized PFMPS (o-PFMPS) for 10 min. Then the substrate was taken out and dried in the air.

Force−extension curves (in brief, force curves) were measured at room temperature (ca. 298 K) with a home-built

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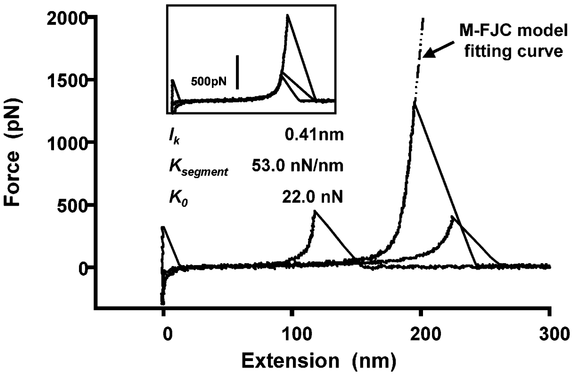

Figure 1. Several typical force−extension curves of PFDMS in THF buffer. One of the force curves is fitted by the M-FJC model curve, shown in the dashed line. Inset: the superposition of the normalized force curves.

SMFS. AFM cantilevers used in the force measurement were commercially available V-shaped Si_3N_4 cantilevers (Park, Sunnyvale, CA), with a spring constant in the range 0.010−0.012 N/m. Force curve measurements were made more than 500 times at different positions of the substrate for each tip/substrate combination. The stretching velocity imposed during the force measurements was about 700 nm s^{-1}. The details of the SMFS experiment have been described elsewhere.[2b,3a,5a] Briefly, polymers were physisorbed onto a quartz substrate. A drop of THF was put onto the substrate and mounted between the cantilever holder and the sample as buffer. By the movement of piezo, the sample was contacted with the AFM tip, and some molecules adsorbed onto the tip, forming a polymer bridge in between. With the separation of substrate and the tip, the polymer chain was stretched and the cantilever would deflect by the elastic force. The deflection−extension curves were recorded and converted later to force−extension curves.[1b]

Results and Discussion

Single-Chain Elasticity of PFDMS. Typical force curves of PFDMS in THF buffer, obtained in different SMFS experiments with different cantilevers, are shown in Figure 1. All the force−extension curves show similar characteristics: the force value rises monotonically with extension, and then the force drops to zero suddenly when a rupture point is reached. The contour length of the polymer chain stretched between the tip and the sample is stochastic (shown in Figure 1) because the molecular weight of polymers is polydisperse, and the anchor points that attach the tip and surface can be anywhere along the polymer chain. To compare the elasticity of the polymer chains with different contour lengths, the force−extension curves are normalized by the extension that refers to the same force value (300 pN).[1,2] All the normalized force curves are superimposed well, as shown in the inset of Figure 1. This fact indicates convincingly that these force signals are from single-chain elongation.

Keeping the loading force lower than the rupture force, we have realized manipulation of the same PFDMS chain. As shown in Figure 2, there is no hysteresis between the consecutive stretching and relaxing curves of the same PFDMS chain, suggesting that the single-molecule manipulation is carried out in equilibrium conditions and the elongation of a single PFDMS chain is reversible.

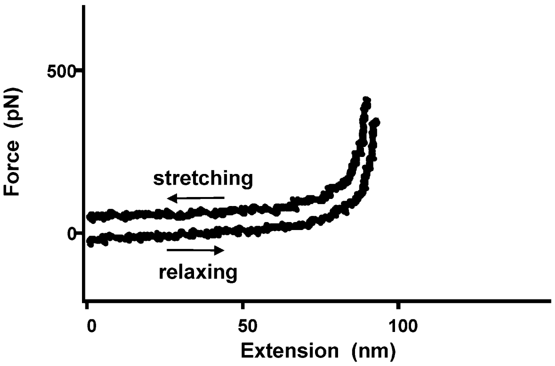

Figure 2. Successive manipulation of a PFDMS single chain, suggesting that the elongation in the experiment is reversible.

We simulate all the force curves and describe the elasticity of single PFDMS chain semiquantitatively using the modified freely jointed chain (M-FJC) model. The M-FJC model, based on the extended Langevin function (see function below), treats a macromolecule as a chain of statistically independent segments.[17] The segments are freely jointed; i.e., there is no restriction to their spatial distribution so that each segment can point in every direction with equal probability.[1b] However, each segment can be deformed under stress:

$$x(F) = \{\coth[(Fl_k)/(k_BT)] - (k_BT)/(Fl_k)\}(L_{contour} + nF/K_{segment})$$

Here, x represents the extension of a polymer chain (end-to-end distance), F is the applied force upon an individual polymer chain, $L_{contour}$ is the contour length of the polymer chain, the Kuhn length (l_k) is the length of the statistically independent segment, n is the number of segments being stretched, which equals $L_{contour}/l_k$, k_B is the Boltzmann constant, and T is the temperature. The deformability of segments is characterized by the segment elasticity, $K_{segment}$. The product of the segment elasticity multiplied by the Kuhn length, K_0, represents the normalized segment elasticity of an individual polymer chain. The elasticity of a single polymer chain is contributed by both entropy and enthalpy. In the low-force regime, the elasticity is mainly governed by entropy, which reflects the contribution of the conformation change of a polymer chain, so-called entropic elasticity. However, in the high-force regime, the elasticity is mainly controlled by enthalpy, which originates from the torsion and rotation of the segments, so-called enthalpic elasticity.

An M-FJC fitting curve of one of the typical curves of PFDMS is shown in Figure 1. All force curves obtained in the SMFS experiments with different cantilevers can be fitted well with a set of narrowly distributed parameters, $l_k = 0.41 \pm 0.01$ nm, $K_{segment} = 53.0 \pm 1.0$ nN/nm, and $K_0 = 22.0 \pm 1.0$ nN, though the contour lengths of the stretched PFDMS chains are different. The narrow distribution of fitting parameters also supports the single-molecule elongation of PFDMS.

Comparison of the Elastic Features between PFDMS and PFMPS. We have performed similar experiments on a single-chain elongation of PFMPS in THF buffer and shown the force curves in Figure 3. From the inset we can clearly see that all the force curves can be normalized and superimposed well. Just similar to PFDMS, we have used the M-FJC model to simulate all the force curves of PFMPS and found that the fitting parameters of elasticity for PFMPS are narrowly distributed: $l_k = 0.36 \pm 0.01$ nm and $K_{segment} = 61.0 \pm 1.0$ nN/nm, so K_0 is 22.0 ± 1.0 nN. Moreover,

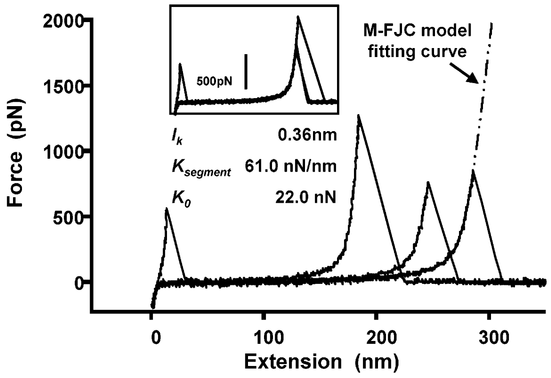

Figure 3. Several typical force–extension curves of PFMPS in THF buffer. One of the force curves is fitted by the M-FJC model curve, shown in the dashed line. Inset: the superposition of the normalized force curves.

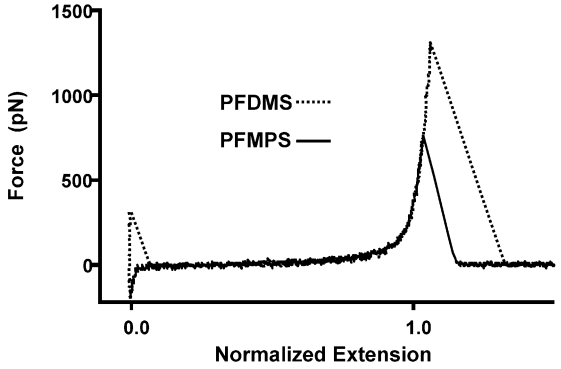

Figure 4. Comparison of the normalized force–extension curves between PFDMS and PFMPS in THF buffer.

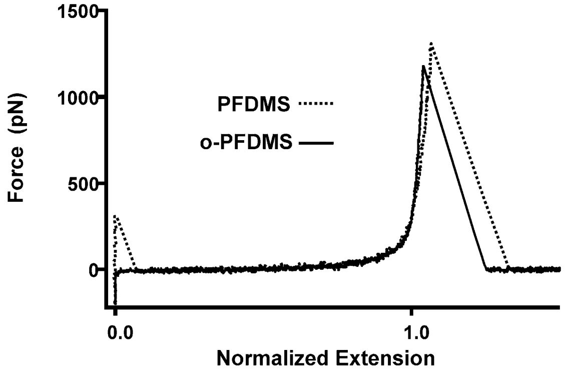

Figure 5. Comparison of the normalized force–extension curves between PFDMS and o-PFDMS in THF buffer.

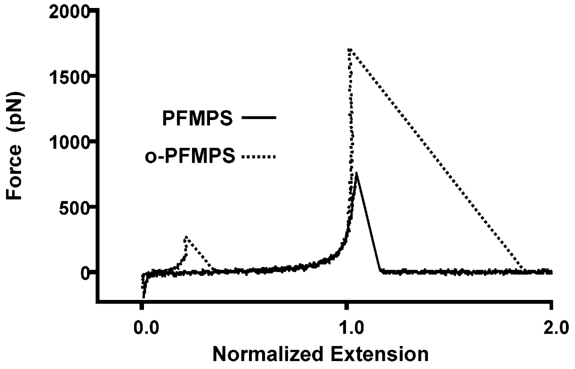

Figure 6. Comparison of the normalized force–extension curves between PFMPS and o-PFMPS in THF buffer.

there is no hysteresis between the stretching and relaxing curves of the same PFMPS strand.

Comparing the fitting parameters of force–extension curves of PFDMS and those of PFMPS, we interestingly find that the single-chain elasticity of the two polymers is almost the same (about 22 nN) in THF buffer. Figure 4 shows the comparison of normalized force–extension curves between PFDMS and PFMPS. The force–extension curves of the two polymers are superimposed well both in the low-force regime and in the high-force regime. These results imply that the two polymers have almost same conformation in THF buffer, and the different side groups bearing on the silicon atoms have little effect on the elongation and rotation of the bonds in the main chain.

Elastic Features of PFDMS and PFMPS after Oxidization. PFS is easily oxidized stoichiometrically using anhydrous $FeCl_3$ in dichloromethane (CH_2Cl_2) solution, and the oxidized forms in the solution can be stable for several days.[14] We have done SMFS experiment on the o-PFDMS and o-PFMPS in THF buffer. The two oxidized polymers have shown different types of single-molecule force curves. Just the same as before oxidization, the normalized force–extension curves of o-PFDMS can be superimposed together well, and so do the curves of o-PFMPS. Moreover, the stretching and relaxing experiments have shown that there is no hysteresis between trace and retrace curves for either of them after oxidization. Since the M-FJC model can fit the two types of force curves well, we have obtained the fitting parameters of the two polymers: for o-PFDMS, $l_k = 0.46 \pm 0.01$ nm, $K_{segment} = 115.0 \pm 1.0$ nN/nm, and K_0 is 53.0 ± 1.0 nN; for o-PFMPS, $l_k = 0.40 \pm 0.01$ nm, $K_{segment} = 500.0 \pm 1.0$ nN/nm, and K_0 is 200.0 ± 1.0 nN. Both good superposition of normalized force curves and narrow distribution of the fitting parameters can confirm that all the force curves are obtained from single-chain manipulation.

Comparing the normalized force–extension curves of PFDMS and o-PFDMS in THF buffer, we can clearly see that they can overlap well in the low-force regime but branch off in the high-force regime: the force curve in the oxidized form is steeper than the normal form, as shown in Figure 5. This difference can be reflected obviously by the M-FJC fitting parameters: the K_0 is 22.0 nN for the normal form of PFDMS; however, it becomes as high as 53.0 nN for the oxidized form. These results indicate that the two forms of the PFDMS single chain present similar entropic elasticity in THF buffer, but the enthalpic elasticity of the oxidized form is larger than that of the normal form.

The PFMPS has shown a similar trend as PFDMS, as shown in Figure 6: the force curve of the oxidized form is steeper than that of the normal form, which suggests a larger enthalpic elasticity of the oxidized form. The difference can be seen also clearly from the M-FJC fitting parameters: the K_0 is 22.0 nN for PFMPS and 200.0 nN for o-PFMPS.

How can the polymers in the oxidized form show larger enthalpic elasticity than that in the normal form? When the polymers are oxidized, the Fc groups in the polymer chains bear positive charges,[13,14] and these charges can be distributed in the polymer chains. Hence, the rising positive charges in the polymer chain can bring the coulomb repulsion and make it more difficult for the torsion and rotation of the repeating units in the polymer chain upon elongation.[18] This should be the reason for the enhanced enthalpic elasticity of the polymers in the oxidized forms. The K_0 of PFDMS is the same as that of PFMPS. In contrast to PFDMS and PFMPS, we find interestingly that the K_0 of o-PFMPS is larger than that of o-PFDMS in THF buffer. We infer that the elastic difference between o-PFMPS and o-PFDMS is probably because of the steric effect of the side groups. The interaction between electron-rich phenyl groups and Fe^{3+} should be stronger than between methyl groups and Fe^{3+} in the oxidized forms. PFDMS and PFMPS exhibit similar enthalpic elasticity before oxidation; however, their difference in enthalpic elasticity can be amplified after oxidation.

Conclusions

We have obtained force spectroscopy on PFDMS and PFMPS before and after oxidation, using AFM-based single-molecule force spectroscopy. The single-chain elasticity of the two polymers is similar to conventional polymers, such as poly(*N*-isopropylacrylamide) (K_0 31 nN) and poly(acrylamide) (K_0 12 nN), though they contain units of Fc. This result supports the previous understanding that the iron atom in Fc acts as a freely rotating "molecular ball-bearing" in polyferrocenylsilane materials.[11,19] The two polymers have shown similar elasticity in normal forms, though bearing different side groups. However, in the oxidized forms the difference in their enthalpic elasticity due to steric effect can be amplified, allowing for differentiating the effect of side groups on single-chain elasticity between o-PFMPS and o-PFDMS. Hopefully, the single-molecule AFM experiment can cast new light on the rational design of PFS materials.

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