

## ARTICLES

Single-Chain Mechanical Property of Poly(*N*-vinyl-2-pyrrolidone) and Interaction with Small Molecules

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The single-chain nanomechanical properties of poly(*N*-vinyl-2-pyrrolidone) (PVPr) and povidone–iodine (PVPr–I<sub>2</sub>) under different solution conditions have been investigated by using an atomic force microscopy based technique—single-molecule force spectroscopy. The force–extension curve (force curve) of PVPr in water is markedly deviated from that obtained in ethanol or tetrahydrofuran, suggesting a different interaction between PVPr and the solvents. Moreover, we have comparatively studied the force signals of PVPr–I<sub>2</sub> and PVPr in an aqueous solution of KI or KI<sub>3</sub> and found that only KI<sub>3</sub> influences the elastic property of PVPr dramatically. These experimental results indicate that there exists a specific interaction between PVPr and KI<sub>3</sub>, which is also supported by Fourier transform infrared data. By the integration of the deviated area between the force curve and the modified freely jointed chain fitting curve, we estimate that the energy needed to destroy the interaction between PVPr and water is 5.3 kT and between PVPr and KI<sub>3</sub> is 3.6 kT per repeating unit, respectively.

## Introduction

Poly(*N*-vinyl-2-pyrrolidone), hereafter denoted as PVPr, is a water-soluble polymer, which displays a strong binding affinity toward small molecules, such as aromatic compounds, phenols, dyes, iodine, and so on. Among those complexed compounds, the PVPr–iodine complex is widely used as a succedaneum for tincture of iodine. Povidone–iodine (PVPr–I<sub>2</sub>) is the name given to the compound formed by the interaction of PVPr and iodine. It is an iodophor commonly used in aqueous antiseptic solutions to increase the solubility of I<sub>2</sub> and is widely used for the disinfection of endoscopes and other surgical instruments.<sup>1,2</sup> Due to its wide use in many fields, the PVPr–I<sub>2</sub> complex has been investigated over the years by several research groups using various techniques, but so far, no consensus has been reached on its molecular structure or on the oxidation state of iodine. Proposed structures for PVPr–I<sub>2</sub> upon complexation include proton fixation between the carbonyl groups of two adjacent pyrrolidone rings<sup>3</sup> and mesomerism of the nitrogen lone pair electrons.<sup>4</sup> The oxidation states of iodine involved in the complex are also unclear, with evidence for complexation of I<sub>2</sub>, I<sub>3</sub><sup>−</sup>, and possibly I<sub>5</sub><sup>−</sup> with PVPr.<sup>3,5</sup> We are wondering if the direct measurement of the behavior of a single polymer chain by single-molecule force spectroscopy (SMFS) may help to understand the complexation system.

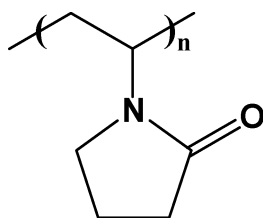
SMFS is based on atomic force microscopy (AFM) and has been developed into a versatile platform for studying intermolecular and intramolecular interactions with extremely high force

sensitivity in recent years.<sup>6–8</sup> This technique has allowed the study of the nanomechanical properties of biomacromolecules as well as synthetic polymers. Until now, by the use of SMFS, many elegant experiments have been performed, such as monitoring of protein unfolding and DNA unzipping,<sup>9–12</sup> single-molecule photomechanical cycles,<sup>13,14</sup> force-induced conformation transition,<sup>15</sup> host–guest complex interactions,<sup>16,17</sup> determination of the rupture force of an individual metallosupramolecular system,<sup>18</sup> single-chain elasticity,<sup>19–23</sup> single-chain desorption from the substrate,<sup>24–29</sup> the behavior of the Rayleigh instability of a polymer globule,<sup>30,31</sup> and even the strength of single covalent bonds.<sup>32</sup> Single-molecule force experiments can be performed under both equilibrium and nonequilibrium conditions by varying the force loading rates in dynamic force spectroscopy.<sup>33,34</sup>

Herein we attempt to investigate the nanomechanical properties of single PVPr chains and the PVPr–iodine complex in different solution conditions by using SMFS, aiming to obtain a better understanding of the interaction of PVPr with iodine and solvent molecules. First, we attempt to study the effect of different solvents, for example, water, ethanol, and tetrahydrofuran (THF), on the force curves of single PVPr chain elongation. Second, on the basis of the comparison of the force curves of PVPr and PVPr–I<sub>2</sub> obtained in different solution conditions, we may deduce whether triiodide (I<sub>3</sub><sup>−</sup>), iodide (I<sup>−</sup>), or molecular iodine (I<sub>2</sub>) is involved in the specific interaction with PVPr chains and even how strong the interaction is. Hopefully, this work can demonstrate a new application of SMFS for investigation of interaction between small molecules and polymers at the solid–liquid interface.

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### SCHEME 1: Primary Structure of Poly(*N*-vinyl-2-pyrrolidone)



### Experiment Section

**Preparation of the Sample for SMFS.** Commercially available poly(*N*-vinyl-2-pyrrolidone) (K90,  $M_n = 360\,000$ , Fluka, Corp.) and poly(*N*-vinyl-2-pyrrolidone)–iodine complex (Aldrich, Corp.) (PVPr– $I_2$ ) were used without further purification in this study. The primary structure of the PVPr is shown in Scheme 1. Potassium iodide (KI) and other reagents are of analytical reagent grade. Deionized water (DI water,  $>18\text{ M}\Omega\text{ cm}$ ) was used when water was involved.

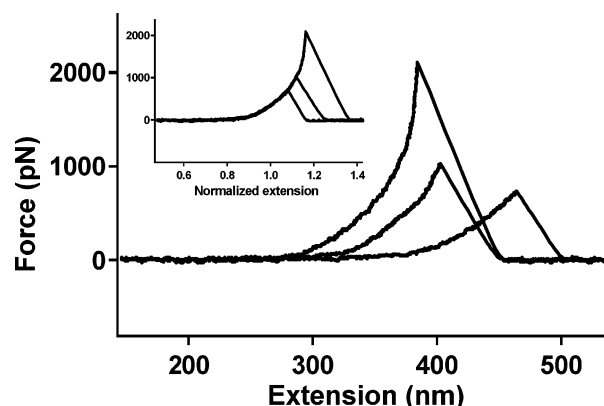
The PVPr and PVPr– $I_2$  samples were dissolved in DI water to a concentration of approximately  $5.0 \times 10^{-3}\text{ mg/mL}$ . The solution was kept at ambient temperature for one week to ensure that the sample was dissolved completely. In our force experiments, quartz slides were used as the substrate. The slides were cleaned by a hot “piranha” solution (7:3 volume ratio, 98%  $H_2SO_4$ /35%  $H_2O_2$ ) and followed by extensive rinsing with DI water before use. About 0.05 mL of sample solution was deposited onto a cleaned quartz slide and incubated for about 30 min. Then the slide was rinsed with DI water to remove the loosely adsorbed molecules. After drying by airflow, the slide was mounted onto the SMFS setup for force measurement. The concentration of the KI solution used for the force measurement was  $1.0 \times 10^{-4}\text{ mol/L}$ , and the aqueous  $KI_3$  solution consisted of  $1.0 \times 10^{-4}\text{ mol/L KI}$  and  $2.0 \times 10^{-5}\text{ mol/L I}_2$ .

**Force Measurement.** All force measurements were carried out on a custom-built single-molecule force spectroscopy setup. Silicon nitride cantilevers from Park Inc. (Sunnyvale, CA) were used. The spring constants of the cantilevers were calibrated by measuring their thermal fluctuation before force measurement,<sup>35</sup> and the measured values were 0.02–0.04 N/m. The experimental details of SMFS have been described elsewhere.<sup>20,36</sup> Prior to the measurements, a drop of liquid, acting as the buffer, was injected between the substrate and the cantilever holder, and then both the substrate and the cantilever were immersed in the buffer. By the movement of the piezo tube, the sample was brought in contact with the AFM tip for ca. 1 s under a contact force of several nanonewtons, allowing some polymer chains to physisorb onto the tip and producing a connective bridge in between. During the separation of the tip and the sample, the polymer chain was stretched and the cantilever deflected. At the same time, a deflection–extension curve was recorded and then converted into a force–extension curve.

**Fourier Transform Infrared (FT-IR) Spectroscopy Measurement.** The FT-IR spectra of PVPr and its mixture with  $KI_3$  were collected on a Bruker IFS 66V instrument equipped with a deuterated triglycine sulfate (DTGS) detector. The aqueous solution of sample was deposited onto the  $CaF_2$  slide, and then the water was removed in a vacuum at ambient temperature.

### Results and Discussion

**Single-Molecule Force Spectroscopy of PVPr in Different Solvents.** To simplify the experiment description, we used



**Figure 1.** Several typical force curves of single PVPr chain elongation with a different contour length in DI water. The inset is the superimposition of normalized force curves.

“object molecule/buffer” to represent the sample and the measurement condition. Several typical force curves of PVPr/DI water, obtained in different SMFS experiments with different cantilevers, are shown in Figure 1. The force rises monotonically with extension, corresponding to the increasing restoring force during the elastic elongation. Then the force rapidly drops to zero, reflecting the desorption of the polymer bridge either from the substrate or from the AFM tip. Due to both the polydispersity of the polymer and the uncontrolled stretching point of the AFM tip, the contour lengths of the polymer segment being stretched vary, as shown in Figure 1. To compare the force curves of the polymer with different contour lengths, the force curves are normalized by their extension corresponding to the same force. After normalization, the force curves can be superposed well, as shown in the inset in Figure 1, indicating that these force signals arise from single-chain elongation.

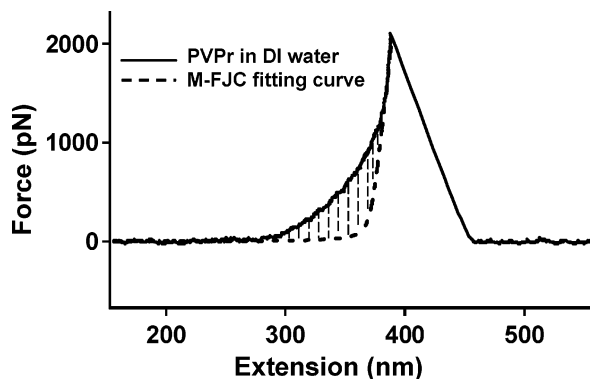
We have used the modified freely jointed chain (M-FJC) model to describe the elasticity of single polymer chains semiquantitatively, although it is only a simple approximation.<sup>6,37</sup> The M-FJC model, which is based on the extended Langevin function (see function below), treats a macromolecule as a chain of statistically independent segments freely jointed together. Herein,  $F$  is the external force applied upon an

$$X(F) = \left\{ \coth\left[\frac{Fl_k}{(k_B T)}\right] - \frac{(k_B T)/(Fl_k)}{(L_{\text{contour}} + nF/K_{\text{segment}})} \right\}$$

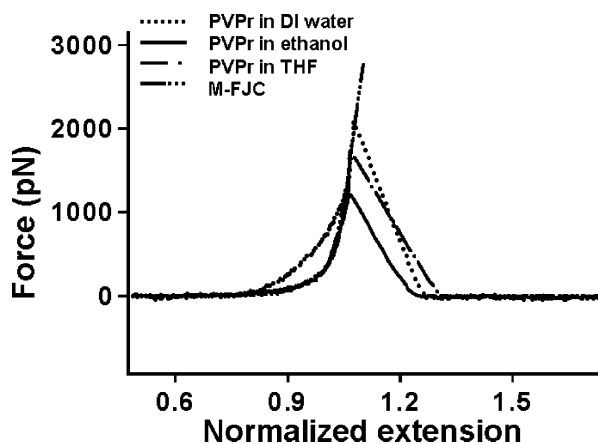
individual polymer chain being stretched,  $X$  represents the extension of the polymer chain (end-to-end distance),  $L_{\text{contour}}$  is the length of the fully extended polymer chain under full extension,  $n$  is the number of segments being stretched,  $k_B$  is the Boltzmann constant, and  $T$  is temperature in kelvin. The deformation of segments is characterized by the segment elasticity,  $K_{\text{segment}}$ . The length of the segment is the Kuhn length ( $l_k$ ). The segments, which are freely jointed together, can be deformed under stress. The Kuhn length and the segment elasticity represent the elasticity of an individual polymer chain. It is reported that the product of the  $l_k$  and  $K_{\text{segment}}$  can be used as normalized segment elasticity,  $K_0$ , which is a standard value for comparison.<sup>6,27</sup> In this way, the M-FJC model can be rewritten as follows

$$X(F) = \left\{ \coth\left[\frac{Fl_k}{(k_B T)}\right] - \frac{(k_B T)/(Fl_k)}{(L_{\text{contour}} + L_{\text{contour}} F/K_0)} \right\}$$

We attempted to fit the PVPr/DI water force curve with the M-FJC model and found that the fitting curve can be only



**Figure 2.** Typical force curve of single PVPr chain elongation in DI water. The dotted line is the fitting curve by using the M-FJC model. Fit parameters are  $l_k = 0.63$  nm and  $K_0 = 41\,580$  pN.



**Figure 3.** Comparison of the normalized force curves of a single PVPr chain elongation in DI water, ethanol, and THF. Fit parameters are  $l_k = 0.31$  nm and  $K_0 = 38\,000$  pN.

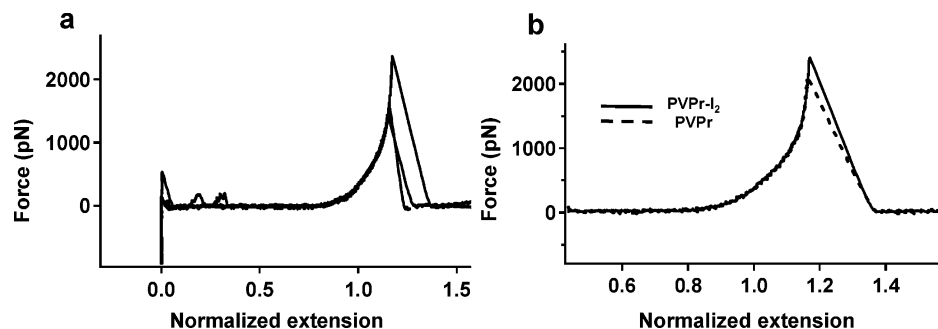
superposed with the force curve in the low or high force regime. The M-FJC model fails to describe the elastic properties of PVPr in the whole force regime though the fitting parameters have been adjusted over a large range. This result indicates that besides the entropic elasticity and torsion barrier, the PVPr chain undergoes another mechanism during elongation causing the deviation from the M-FJC model. In the system of PVPr, every repeating unit of the polymer bears a carbonyl group and amido bond and they can also strongly interact with water molecules via hydrogen bonding, as confirmed by IR spectroscopy<sup>38</sup> and sorption isotherm.<sup>39</sup> Thus, we believe that the deviation between the force curves of PVPr/DI water and the M-FJC model fitting curve should be attributed to the formation of hydrogen bonds between the solvent molecules and polymer.

To better understand the interaction between PVPr and solvents, we have performed similar experiments that use pure ethanol as a buffer. In this case, we find that the M-FJC model is able to fit the PVPr/ethanol force curve in the whole force regime (Figure 3). It is expected that the ethanol molecules can also interact with PVPr chains via a hydrogen bond.<sup>40</sup> However, the force curves of PVPr chain elongation obtained in water and ethanol are distinctly different (Figure 3). These experimental data may indicate a different hydrogen-bonding structure between polymer and solvent molecules. When the water and ethanol molecules are compared, the difference between the two solvents lies in the number of hydrogen bond donors: each water molecule has two hydrogen bond donors whereas each ethanol molecule only bears one. That is to say, one water molecule can interact with two repeating units of PVPr in DI water, whereas in case of ethanol, only one hydrogen bond can be

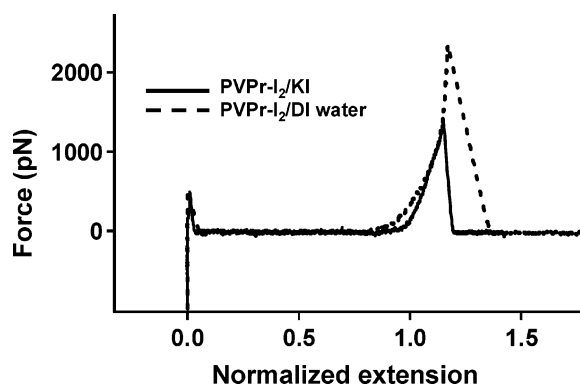
formed with PVPr chains for one solvent molecule. Therefore we think the water molecules may link the repeating units of PVPr together by forming a water bridge between the carbonyl groups of pyrrolidone rings in DI water. There is a probability that water molecules may bridge with pyrrolidone rings from different chains in aqueous PVPr solution. However all the force signals we have analyzed here are from single-chain manipulation, which is supported by the good superposition of the normalized force curves. The distance between the pyrrolidone rings is increased upon stretching of the polymer chain. When the chain is elongated to a certain extent, the water bridge is ruptured, which needs additional energy beyond chain elasticity to destroy the hydrogen bonding. It is expected that the area between the experimental force curve and the M-FJC model corresponds to the energy required to destroy the suprastructure in a polymer chain during chain elongation. We managed to integrate the shadow area in Figure 2 and found that the average energy is approximately 5.3 kT per repeating unit. It is reported that the binding energy between the PVPr and water is about 32.4 kJ/mol, which was obtained from an ab initio calculation.<sup>41</sup> Considering the fact that it can only destroy one hydrogen bond for two pyrrolidone rings during the PVPr chain being stretched, we estimate that the binding energy between PVPr and water is approximately 26.3 kJ/mol. These two results are comparable to some extent. In the case of PVPr in ethanol, no energy is needed to destroy such an interaction between the polymer and the solvent during elongation, so the force curve of PVPr/ethanol can be fitted well with the M-FJC model in the whole force regime.

To prove further our speculation about the water bridges between the pyrrolidone rings of the polymer, we have used THF, which bears no hydrogen bond donor, as a buffer for the force measurement. Because of the absence of hydrogen bond donors in THF, the solvent cannot form hydrogen bonds with PVPr. One normalized force curve of PVPr obtained in THF is shown in Figure 3. Interestingly, the force curve can be superposed well with the force curve obtained in ethanol in the whole force regime. On the basis of the comparison of the force curves of PVPr obtained in these three buffers, we can conclude that the water bridges between the repeating units of the polymer via hydrogen bonds affect the nanomechanical properties of PVPr chains and induce the deviation between the force curves of PVPr/DI water and the M-FJC fitting curve. In the case of ethanol as the buffer, although there exists hydrogen bonds between the PVPr and the solvent, the elasticity of the polymer chain evidently is not affected. Consequently, the force curve in ethanol is the same as that obtained in THF, which cannot form a hydrogen bond with the polymer chain.

**Single-Molecule Force Spectroscopy of PVPr–I<sub>2</sub>.** To obtain more insight into the interaction of PVPr with iodine, we have studied the force spectroscopy of the PVPr–I<sub>2</sub> complex in DI water. As shown in Figure 4a, the good superposition of the normalized force curves is indicative of single-chain stretching. However, to our surprise, there is no difference between the force curves of PVPr and PVPr–I<sub>2</sub> in DI water; see Figure 4b. That is to say, the molecular iodine (I<sub>2</sub>) does not affect the elasticity of PVPr chains dramatically. Cheng et al. have confirmed the specific interaction between pyrrolidone rings and iodine in the PVPr–I<sub>2</sub> complex using <sup>13</sup>C NMR, but it seemed hard to determine the oxidation state of the iodine.<sup>42</sup> By the use of Raman spectroscopy, de Faria et al. have found the interaction between the PVPr and iodine depends on the method used in the sample preparation.<sup>4</sup> To clarify the different oxidation states of iodine in the complex, an aqueous KI solution



**Figure 4.** (a) The normalized force curves of a single PVPr- $I_2$  chain elongation in DI water. (b) Comparison of the normalized force curves of single-chain elongation of PVPr- $I_2$  and PVPr obtained in DI water.



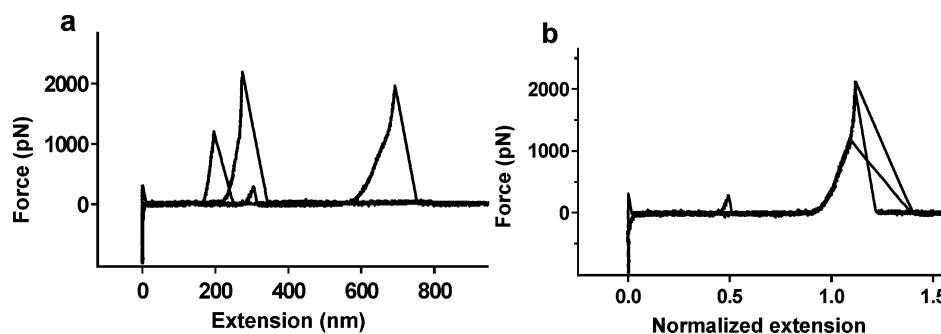
**Figure 5.** Comparison of the normalized force curves of a single PVPr- $I_2$  chain elongation obtained in DI water and KI solution.

was used as the buffer for the force measurement. When we compared the normalized force curves of PVPr- $I_2$  in DI water and in KI solution, we found that the two curves can only be superposed well in the high force regime and that there is a clear deviation in the low force regime, as shown in Figure 5. It is well-known that the iodide anion ( $I^-$ ) can combine with molecular iodine ( $I_2$ ) to form triiodide ( $I_3^-$ ) in aqueous solution. Hence we think that the deviation of the two normalized force curves in the low force regime would relate to a specific interaction between PVPr and  $I_3^-$ .

To provide further evidence for the above speculations on specific interactions between PVPr and triiodide, we used the PVPr and the aqueous  $KI_3$  solution as a buffer to repeat the experiment. Several typical force curves of PVPr in aqueous  $KI_3$  solution are shown in Figure 6a. Similarly, we have normalized these force curves, and the good superposition of the normalized force curves (Figure 6b) indicates that single molecule manipulation is realized. When the normalized force curves of PVPr/ $KI_3$  and PVPr- $I_2$ /KI are put together, we find they can be superposed well into the whole force regime (Figure

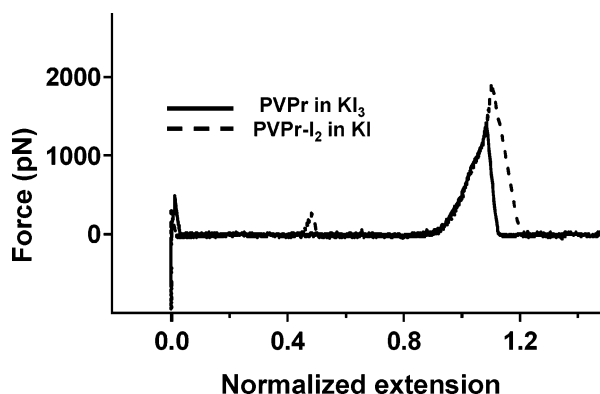
7). These results confirm the hypothesis that it is the triiodide strongly interacting with the PVPr in aqueous condition and the interaction between the PVPr and  $I_3^-$  affects the chain elasticity dramatically. We tried to fit the PVPr/ $KI_3$  force curve by using the M-FJC model, and the result is shown in Figure 8. There is a large deviation between the force curve and the fitting curve. By integration of the deviation area between the force curve of PVPr in  $KI_3$  and the M-FJC fitting curve, we found that the average energy needed to destroy the interaction between the PVPr and  $I_3^-$  during the chain elongation is approximately 3.6 kT per repeating unit. The trace amount of  $I_3^-$  influences the nanomechanical property of the single PVPr chain greatly. The evident deviation between the force curves of PVPr/DI water and PVPr/ $KI_3$  indicates that PVPr exists prior to combining with  $I_3^-$  than with water, and the interaction between the PVPr and  $I_3^-$  is dominant when  $KI_3$  exists in aqueous solution. Because of the existence of KI in  $KI_3$  solutions, there is another possibility that the deviation is caused by salt effects. Therefore, the KI solution was used as a buffer for the force measurement, and the force curves of PVPr obtained in KI solution and DI water show no difference in the whole force regime, as shown in Figure 9. Thus we can exclude the possibility that the deviation is caused by the KI in  $KI_3$  solution.

To draw conclusions from the mechanical data to a structural property is indirect; thus we used FT-IR to study the interaction between PVPr and  $KI_3$ . As shown in Figure 10, we measured the IR spectra of PVPr and its mixture with  $KI_3$  and highlighted the spectral changes of the carbonyl stretching vibration band. Curve a is the IR spectrum of the PVPr film, and a band at approximate  $1680\text{ cm}^{-1}$  is attributed to the carbonyl stretching mode. Curve b is the IR spectrum of PVPr under the existence of excess  $KI_3$ . By comparing curves a and b, we can clearly see that the carbonyl band undergoes an apparent shift to the longer wavelength ( $1669\text{ cm}^{-1}$ ) as the addition of  $KI_3$ . This result indicates that there exists a specific interaction between

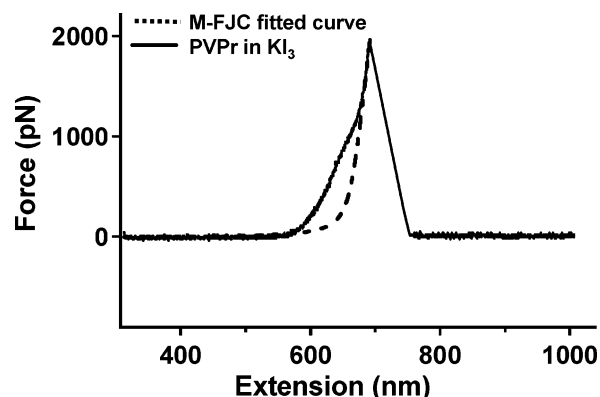


**Figure 6.** (a) Typical force curves of a single PVPr chain elongation obtained in  $KI_3$  buffer solution. (b) The superimposition of the normalized forces in Figure 6a.

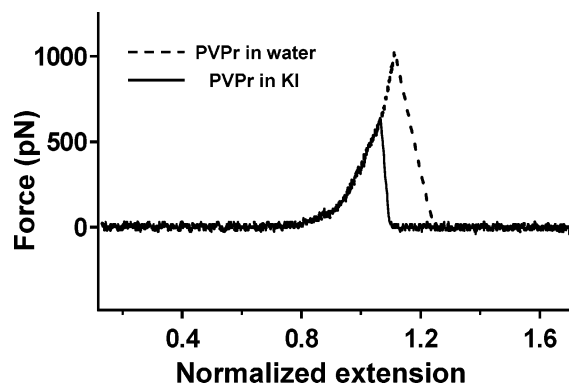




**Figure 7.** Superimposition of normalized force curves of PVPr in aqueous  $\text{KI}_3$  solution and the normalized force curve of PVP- $\text{I}_2$  obtained in aqueous KI solution.



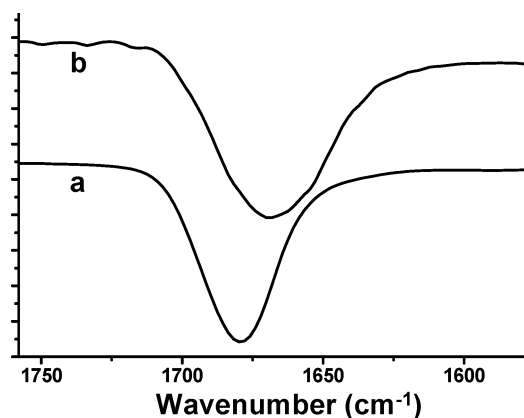
**Figure 8.** Typical force curve of a single PVPr chain elongation obtained in  $\text{KI}_3$  solution and the fitting curve by using the M-FJC model. Fit parameters are  $l_k = 0.57$  nm and  $K_0 = 42\,180$  pN.



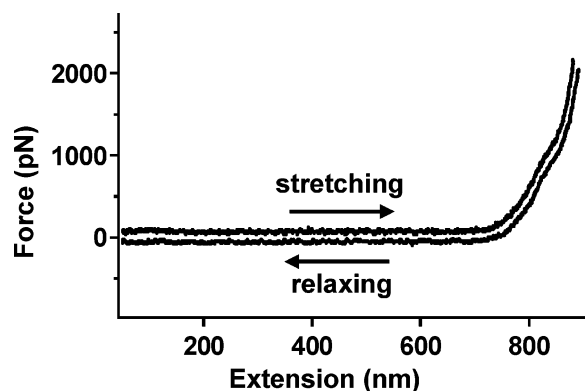
**Figure 9.** Normalized force curve of PVPr in DI water and the normalized force curve of PVP obtained in aqueous KI solution.

the PVPr and  $\text{KI}_3$ , which is consistent with the conclusion from the mechanical data of PVPr chain by using single-molecule force spectroscopy.

By keeping the stretching force lower than the rupture force, we have repeatedly stretched and relaxed a unique polymer chain. Figure 11 shows a consecutive trace–retrace pair of PVPr/ $\text{KI}_3$ . No hysteresis is observed between the stretching and relaxing traces, indicating that the single-chain manipulation is carried out under equilibrium conditions. In other words, the pyrrolidone rings complexed with iodine and the free-standing pyrrolidone rings are in fast and reversible exchange. This conclusion is consistent with the previous findings using  $^{13}\text{C}$  NMR.<sup>42</sup>



**Figure 10.** FT-IR spectra of PVPr and its mixture with  $\text{KI}_3$  in 1750–1600  $\text{cm}^{-1}$ : curve a, PVPr film; curve b, PVPr film under the existence of excess  $\text{KI}_3$ .



**Figure 11.** Stretching and relaxing traces of the identical PVPr chain in aqueous  $\text{KI}_3$  solution. For clarity the two curves are offset.

## Conclusions

In this article, we have studied the interaction between PVPr and small molecules by using SMFS. Although there are many reports on the interaction between PVPr and water or ethanol by using spectrum analysis, our results based on SMFS can also clearly indicate the different interactions that are consistent with published literature. Thus, we have come to use SMFS to clarify the interaction between PVPr and different species of iodine. We found that only the triiodide anion ( $\text{I}_3^-$ ) affects the chain elasticity of PVPr markedly, whereas  $\text{I}_2$  or  $\text{I}^-$  has no influence. These results indicate that there exists a specific interaction between triiodide and PVPr chains, which is also supported by FT-IR data.

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