Single Polymers

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Large Mechanical Response of Single Dendronized Polymers Induced by Ionic Strength**

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For about a decade, researchers have been unraveling the mechanical properties of single polymer chains. DNA helices were found to respond to stretching forces in a nontrivial fashion depending on their twisting and zipping states.[1,2] Conformational transitions were identified to determine the characteristic mechanical response of elastic proteins (e.g., titin, tenascin, ankytrin)[3–5] and of polysaccharides.[6–8] Mechanical properties of simple neutral and charged polymers of known structure were investigated in detail and compared with ab initio calculations.[9–13]

To use single polymers as building blocks in molecular machines and devices,[2,14] one must be able to control their mechanical response.[6,8,9,12,15] For elastic proteins, impressive changes in their elongation by factors of 2–3 were reported in the force range 0.1–0.3 nN as a result of unfolding of individual domains.[3–5] Amylose shows changes in its elongation of 10–20 % in a similar force range. These changes were interpreted in terms of conformational transitions of the pyranose rings.[6,8] Although synthetic polymers can be tuned in a reversible fashion by optical excitation,[12] redox properties,[15] and the nature of the solvent,[9] the changes in the elongation that were obtained are only 5–15 % and were observed for forces below 0.1 nN. Synthetic polymers featuring a more significant response, especially at larger forces, have not been described so far.

A larger mechanical response of synthetic polymers could be obtained by modifying their stiffness. Although the persistence length of linear polyelectrolytes as measured by light scattering can be tuned substantially through the ionic strength of the surrounding aqueous medium,[16] no substantial change in chain elasticity was observed.[10,11] This surprising feature was explained by a scale dependence of the measured persistence length.[17] The stiffness of comblike polymers, such as bottle-brush[18,19] and dendronized polymers,[20,21] can be varied by increasing the packing density of the side chains. Bottle-brush polymers may seem promising because of their wide structural variability and appropriate mechanical properties,[18,19] but the rapid decrease of the side-chain monomer density away from the backbone and the currently inevitable polydispersity of the side chains will hardly lead to the desired sensitivity of the force response upon external parameters.

Dendronized polymers appear to be more promising in this respect, as the side dendrons can be grown with low polydispersity. They induce a high packing density near the polymer backbone and lead to an increase of the persistence length with generation.[22,23] Therefore, we suspect that elastic properties of dendronized polymers might show a strong response to external parameters, such as solvent composition or temperature.

This Communication confirms this suggestion by demonstrating that the elasticity of highly charged dendronized polymers shows a large response to ionic strength in aqueous solutions. This study uses polymethacrylate-based dendronized polymers terminated with amine groups of different generations (PGn, $n = 1$–4, Figure 1).[20,22,23]

The mechanical properties of individual dendronized polymers were probed by atomic force microscopy (AFM) in force spectroscopy mode.[5,10,12,18,24] This technique measures the stretching force of a polymer chain bridging the AFM tip and the substrate (Figure 2). Dendronized polymers grafted onto the AFM tip are likely to attach covalently to the substrate upon contact between the tip and the substrate. When a polymer chain bridging the tip and the substrate is pulled by the AFM tip, a characteristic spike is detected in the retraction part of the force curve.

Typical force curves measured with PG3 in KCl solutions at pH 4 are shown in Figure 2 a. Each spike corresponds to the stretching of an individual polymer chain. The left hand side of the spike is determined by the nonlinear stretching response of the polymer chain, and the arrow on the right hand side indicates the jump out due to the mechanical instability when the stretched polymer detaches from either surface or ruptures. These stretching events occur at different distances from the surface. These distances reflect the different contour lengths of the polymer segments bridging the tip and the substrate. They must be smaller than the contour length of the entire polymer, but otherwise follow a broad statistical segment-length distribution. One further observes a widening of the spikes with increasing pulling distance. This feature reflects the softening of a polymer chain with increasing segment length, and is fully analogous to an ordinary spring, which also weakens with increasing length.

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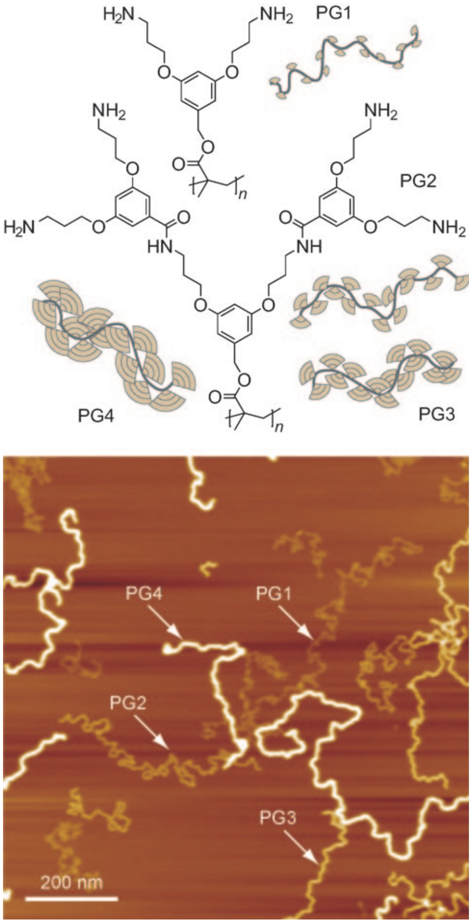

Figure 1. Top: Polymethacrylate-based dendronized polymers terminated with deprotected amine groups of different generations PG*n* used in this study. Bottom: Tapping-mode AFM height image showing polymers of different generations with protected amine groups adsorbed on mica.

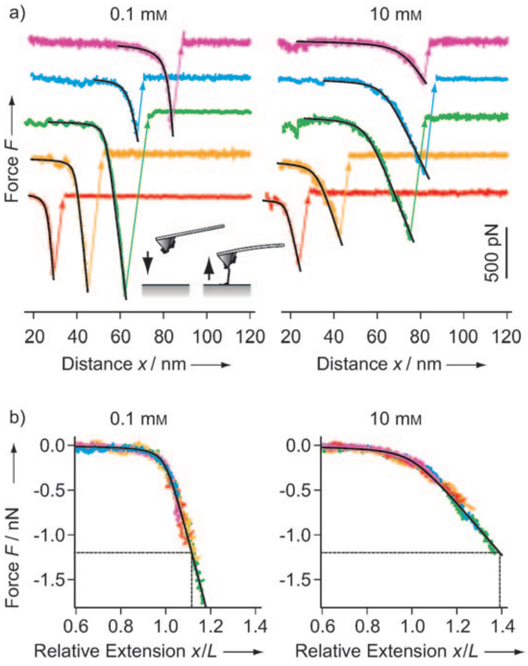

Figure 2. Probing the mechanical response of single PG3 dendronized polymers and tuning it by the ionic strength from 0.1 mM (left column) to 10 mM KCl (right column). The inset illustrates a scheme of the single-molecule force experiment. Solid black lines are best fits with the FJC model. a) Individual force curves showing single-molecule stretching events versus distance. b) Master plot of the force versus the relative extension. The dotted lines indicate the extensions at the reference force of 1.2 nN.

The large response of mechanical properties of dendronized polymers with the ionic strength is already evident from the individual force curves shown in Figure 2a. At a given separation, the spikes are substantially narrower at 0.1 mM than at 10 mM. To quantify this response, the force F versus the extension x was fitted to the high-force limit of the freely jointed chain (FJC) model including chain elasticity [Eq. (1)],[13,25,26] where L is the contour length of the polymer segment, kT is the thermal energy, ℓ is the apparent Kuhn length, and K is the elasticity constant. For forces larger than the sensitivity of our AFM setup of about 0.02 nN, this simple high-force limit is valid and numerically equivalent to other FJC models used previously.[1,4,9,27,28] The measured force–extension curves are consistent with this simple model and scale to a common master curve when plotted as a function of relative extension x/L (Figure 2b). This coincidence represents strong evidence that single polymer chains are being pulled. Indeed, increasing the ionic strength from 0.1 mM to 10 mM leads to substantial softening of the PG3 chain, with a change in the relative extension from 1.11 to 1.39 at a force of 1.2 nN. This modification in the ionic strength leads to a large change of 25% in the elongation. Since the force curves were found to be independent of the pulling velocity, the extension process is reversible.[24] Further details are given in the Supporting Information.

$$\frac{x}{L} = 1 - \frac{kT}{\ell F} + \frac{F}{K} \tag{1}$$

The fitted parameters were compared with results from additional measurements for other ionic strengths and generations (Figure 3). For the higher-generation polymers, the elasticity constant K and the apparent Kuhn length ℓ decrease with increasing ionic strength and increase with the generation of the side chain. These values suggest a substantial stiffening of the chain with decreasing ionic strength and

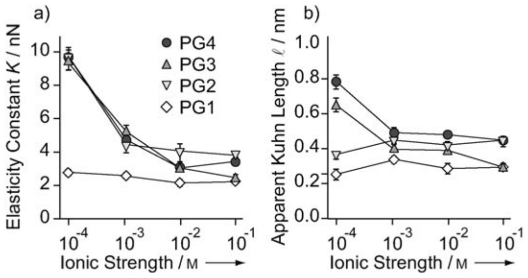

Figure 3. Parameters characterizing the mechanical properties of dendronized polymers versus ionic strength. a) Elasticity constant and b) apparent Kuhn length. Both parameters were found to be independent of the contour length. Solid lines serve to guide the eye.

increasing generation. An analogous FJC model was used earlier to rationalize the stretching response of neutral poly(*p*-phenylene) dendronized polymers in various organic solvents.[29] For generation 2, these authors report apparent Kuhn lengths between 0.3–0.4 nm and elasticity constants of 25–35 nN. Although the reported Kuhn lengths are similar to the present findings, the elasticity constants are somewhat larger. For these poly(*p*-phenylene) dendronized polymers, however, variations in the elastic properties in different solvents were insignificant.[29]

The presently observed apparent Kuhn lengths are at least a factor of 10 smaller than the persistence lengths observed by AFM.[23] For other charged polymers, similar discrepancies were described between Kuhn or persistence lengths derived from single molecule pulling experiments and light scattering.[10,17] The main reason for these discrepancies is that the persistence length determined by light scattering includes the electrostatic part, whereas the pulling experiments mainly probe the bare persistence length.

Our key finding is the substantial variation of the chain elastic properties with the ionic strength, especially for PG3 and PG4. The chains soften strongly with increasing ionic strength. The difference in the extensions between 0.1 mM and 100 mM for PG3 is about 30 % at 1 nN, whereas for PG4 a change of about 25 % was observed. To our knowledge, such a large response, especially in the nN force range, has not been reported. The response for PG2 is somewhat weaker, and it is almost inexistent for PG1. The behavior of PG1 reminds us of a simple polyelectrolyte.

We suspect that the substantial stiffening of the chain is caused by electrostatic interactions between the numerous charged primary amino end groups of higher-generation dendrons. Since the density of these groups strongly decreases with decreasing generation, it does not astound us that a much weaker response was observed for PG1. The present finding is also in line with the known weak influence of the ionic strength on linear polyelectrolytes.[10,11] A similar transition between a flexible conformation for PG1 and a more rigid structure of PG2 was found by dynamic light scattering measurements.[30] The increase of the elasticity constant with decreasing ionic strength probably originates from the high charge density of the polymers and an increasing importance of electrostatic interactions. The weak generation dependence of this parameter may originate from a balance between the mechanical stiffening due to increasing chain thickness and a corresponding decrease in the electrostatic forces due to smaller curvature of the double layer.

We have demonstrated herein that mechanical properties of single dendronized polymers can be strongly modified in aqueous solutions. The effect is illustrated with cationic dendronized polymers and shows their considerable softening with increasing ionic strength. We have shown for the first time that mechanical properties of single polymers can be substantially modified by changing the ionic composition of aqueous solutions. With this proof of principle, we expect that similar effects could be observed with pH value, metal ions, solvent quality, or temperature. By systematic variation of the functional groups and the chemical nature of the side dendrons, it might be possible to design polymers that feature an even larger response. Given the possibility to tune the elasticity of dendronized polymers significantly through the presence of specific ions in aqueous solutions, such polymers may become ideal building blocks for single-molecule machines, especially as nanoactuators, or molecular motors.[12,31,32] These results illustrate the advantage of dendronized polymers, which rely on the same chemistry, but at the same time allow variation of the number of functional groups per main chain of repeat unit, and thereby lead to systematic variation of the mechanical response.

Experimental Section

Polymethacrylate-based dendronized polymers of different generations (PGn, $n = 1$–4) terminated with amine groups were synthesized through the attach-to route and their structure perfection was quantified as described earlier.[23] The polydispersity of the backbone chains was $1.4 < M_w/M_n < 1.8$, where M_w and M_n are the weight and number average molecular masses, repectively. The polydispersity of the side dendrons is less than 1 % when expressed as the deviation from the theoretical number of 2^n of the amine groups per repeat unit.

The mechanical properties of the polymers were probed with a closed-loop atomic force microscope. Dendronized polymers were attached to cantilevers by silanizing the silicon tips with (3-glycidoxypropyl)dimethylethoxysilane and by incubating them in aqueous solutions at room temperature at pH 4.0 for 1–2 h. In this way, polymer chains are grafted to the tip by a nucleophilic ring-opening reaction of the epoxy group on the tip surface and the amino groups on the polymer.[11] Further experimental details are given in the Supporting Information.

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