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Stimuli-Sensitive Polymer Gels That Stiffen upon Swelling

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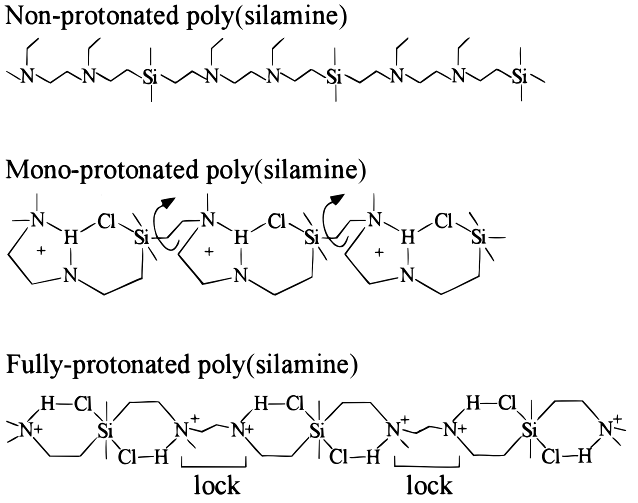
Materials that respond to external stimuli to change their properties are of increasing interest. Particularly extensive studies have been carried out for acrylic hydrogel, which undergoes shape and swelling transition upon hydration. Phase transition in such stimuli-sensitive hydrogels is primarily driven by a persistent length transition, viz., a transition from the coil with a short persistence length to one with a long persistence length, which arise from changing interactions between polymer networks and solvent.[1−8] In a gel's swollen state, each polymer chain is isolated by solvent molecules and is therefore exposed as a single molecular unit to tension and shear forces produced during a gel deformation process. In the case of polyelectrolyte gel, modulus decreases with increasing swelling degree at comparatively low values of solvent content. An upturn in modulus increasing with rising solvent content at high swelling state was reported. It was interpreted in the terms of non-Gaussian elasticity of highly stretched network chain.[9] Hence, poor hydrogel mechanical properties especially in the elastic region of Gaussian theory consistently limit their applications.[7] Biological materials are usually of soft and wet composition like hydrogels. Their mechanical properties can be changed rapidly in response to external stimuli. For example, sea cucumbers stiffen their bodies when touched and are no longer deformable. Such change in mechanical property of the tissue may be the result of a viscosity change in the extracellular materials within the tissue caused by the binding of calcium ion to proteinous structure.[10] In this regard, a novel concept is revealed to design hydrogels with stiffened properties at swollen state.

Here, we report a novel stimuli-sensitive polymeric hydrogel system that stiffens upon swelling based on a reversible rod−globule transition in a network polymer. The chemistry is based on the silicon-based polymer, poly(silamine), comprising alternating units of *N,N′*-diethylethylenediamine and 3,3-dimethyl-3-silapentamethylene.[11]

Poly(silamine) was prepared via anionic polyaddition reactions between difunctional vinylsilane and diamine in the presence of lithium alkylamide as reported.[11] Poly(silamine) is terminated at both ends by secondary amines which are easily converted to acrylamide groups by reaction with acryloyl chloride. These reactive end groups permit chemical cross-linking of polymers to form a gel as follows: 3 g of poly(silamine) (1.5 mmol), 0.44 g of pentaerythritol tetrakis(2-mercaptopropionate) (0.9 mmol), and 0.08 g of 2,2-dimethoxy-2-phenylacetophenone (0.3 mmol) were dissolved in 3 mL of THF. The mixture was injected into a glass cell (3 cm × 3 cm × 0.5 cm) and irradiated with 3 mW/cm^2 UV light for 5 min. Poly(silamine) gel formed was immersed in a large amount of acetone to remove the non-cross-linked polymer and initiator.

Scheme 1. Plausible Poly(silamine) Conformations on Protonation and Anion Binding[11]



Poly(silamine) showed a unique phase transition property in response to the degree of protonation of its amino groups in aqueous media as we revealed previously.[11b] The unprotonated poly(silamine) is insoluble in water. While increasing acidity protonates both backbone nitrogens, yields the soluble charged form. Additionally NMR investigation suggested that interactions between the protonated *N,N′*-ethylenediamine unit and silicon mediated by counteranions as shown in Scheme 1 are plausible, because silicon atoms in the main chain of poly(silamine) possess weak Lewis acidity.[11c] Such chelation together with protonation of poly(silamine) suppresses main chain rotation, resulting in an unprecedented reduction in the chain flexibility and network elasticity. This is supported by changes observed for the glass transition temperature of this polymer as a function of backbone protonation from −85 °C (nonprotonated form) to +80 °C (full protonation form by H_2SO_4).[11c]

Poly(silamine) hydrogels in aqueous media exhibited reproducible swelling/deswelling behavior in response to the protonation degree (α) of the network. It is widely accepted that swelling equilibria in ionic gels result from a balance of the following factors: (i) the free energy of mixing of the network chains with the solvent, (ii) ion osmotic pressure, and (iii) the elastic retractile response of the expanding gel network.[8] The volume transition in stimuli-sensitive ionic gels based on vinyl polymers with side-chain dissociative groups (e.g., poly(acrylic acid)) is driven by the persistence length transition. At the swelling equilibrium, the osmotic pressure is balanced by the elastic pressure because of the stretching of network.[9] Poly(silamine) gel network chains expand and rigidify their conformation on protonation and anion binding,[11] which induce the gel swelling consistently. We have previously reported that poly(silamine) gel,

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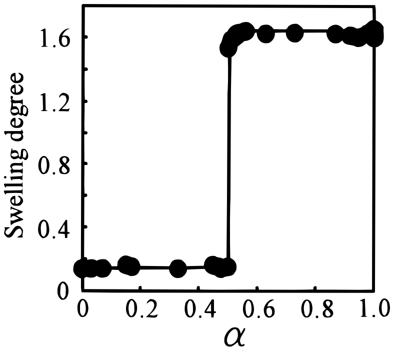

Figure 1. Changes in gel swelling as a function of degree of protonation of poly(silamine) gel in 5.0 M NaCl solution. The dried disk was first immersed in a pH 2.0 aqueous solution and allowed to reach equilibrium swelling, followed by successive bathing in a series of solutions with increasing pH up to 9.0. The disk was bathed in each solution until it reached a constant weight. The disk was then successively bathed in a series of solutions with decreasing pH from 9.0 to 2.0 in a similar manner. The swelling/deswelling cycle was repeated several times to determine the reproducibility.

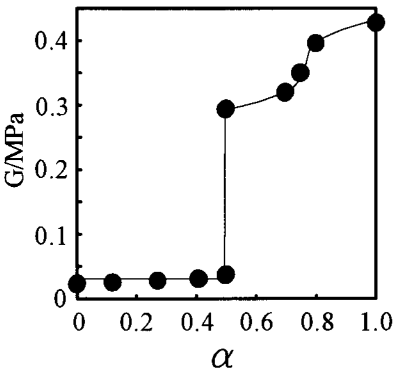

Figure 2. Changes in the shear moduli of poly(silamine) hydrogel at frequency (ω) of 0.01 Hz as a function of the protonation degree in 5.0 M NaCl solution. Dynamic rheological measurements were obtained using a Rheometric Scientific ARES rheometer operated in the parallel plate geometry, with 25 mm diameter plates. The dynamic storage (G') and loss (G'') moduli of poly(silamine) hydrogel were measured as a function of angular frequency (ω) by the change from 0.01 to 10 Hz at 30 °C with a strain of 0.5%.

which was prepared by the reaction of the amino-ended polymer and toluene-2,4-diisocyanate to form the isocyanate-ended poly(silamine) followed by the cross-linking reaction with trimethylolethane, showed extremely high swelling degree (16 200%) when soaked in 0.01 N HCl, while the gel showed moderate swelling in good organic solvents such as THF (1840%) and methanol (2160%).[11d] The swelling in organic solvents should be dominated by the balance between solvent–network interaction (positive force) and rubber elasticity of the network (negative force). On the contrary, the rigid expanded conformation of the network decreased the negative contribution of the rubber elasticity. The contribution of this rubber elasticity factor in addition to the other two positive factors, viz., positive solvent–network interaction and the ionic osmotic pressure, increased the swelling degree significantly.

To avoid the ionic osmotic pressure effect, the swelling characteristics were investigated under high ionic strength. As shown in Figure 1, an abrupt discontinuous change in the equilibrium gel swelling degree of poly(silamine) in aqueous media was observed at a critical pH 7.8, corresponding to protonation degree $\alpha = 0.5$.[11c] Gels swell 160% even in a solution with an extremely high concentration, 5 M NaCl. With the protonation degree is above 0.5, no increasing in swelling took place, indicating that the gel is in maximum swelling. Effect of further increase in the counterion due to the second protonation of the ethylenediamine units is negligible when the gel is in the swollen state. In the case of polyacrylic hydrogel, the swelling degree increases with increasing ionization degree even above the transition point. This is easily explained by the increase in the ionic osmotic pressure against the retractile force from the rubber elasticity.[9] On the contrary, when the phase transition takes place in the case of poly(silamine) gel, the network becomes rigid and fully expanded conformation.[11] This causes the maximum swelling of the gel. Once the rigid expanded network skeleton was formed, the osmotic pressure of the gel interior may not influence significantly the swelling degree. When α is below 0.5, deprotonated units start free rotation around the main chain to make it more flexible than that at $\alpha = 0.5$, which increases hydrophobic interaction around nonprotonated ethylenediamine units to result in a shrinkage of the polymer chains from their expanded conformation.[11]

Because the swollen state of the poly(silamine) gel should be rigid and expanded network due to the amine protonation along with the anion binding as shown in Scheme 1, it is anticipated that the gel becomes stiff when it swells. As displayed in Figure 2, the shear moduli (G) of poly(silamine) gel increased abruptly at the phase transition point ($\alpha = 0.5$). It should be noted that the gel swells at this point, and it contains 62% of water. This phenomenon is completely opposite from common stimuli sensitive gels.[9] It is interesting to note that the shear moduli increase again at $\alpha = 0.75$, which corresponds to the second amine protonation point shown in Scheme 1. Rotation locking around the $N^+-CH_2CH_2-N^+$ unit may influence the stiffness of the gel, though the gel swelling degree did not change at all at this point.

In conclusion, the new silicon-based polycation, poly(silamine), exhibited reversible rod–globule transitions with minute changes in environmental stimuli such as pH. The chemically cross-linked poly(silamine) xerogel is an elastic material, exhibiting a shear modulus of ca. 30 kPa. By contrast, its hydrogel shows increasing modulus with increasing water content to more than 60%. The shear modulus of the water-swollen gel is ca. 400 kPa. This increased stiffening with increased solvent is a striking contrast with other stimuli-sensitive gels reported that consistently soften as they swell in water at comparatively low swelling degree as we discussed above.[9] These unique mechanical properties are proposed to arise from polymer structural (rod–globule) transitions that increase gel flexural rigidity with increasing hydration and decreasing pH. Such kinds of gels are very promising candidates for the use as actuators in artificial muscle as well as a pump system in controlled drug release.

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