# Rubber Elasticity Transition of Poly(silamine) Induced by Ionic Interactions

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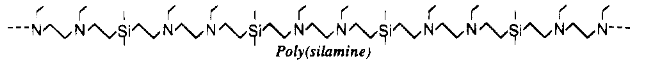
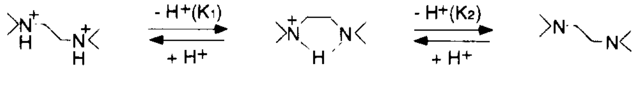
A polypeptide, which is one of the main components of protein molecules, shows diverse conformations through hydrogen bonding, such as $\alpha$-helix and $\beta$-sheet.[1] The well-organized conformation-like $\alpha$-helix can be converted by a minute change in environmental conditions such as solvent, temperature, and composition.[2] Such a helix–random coil transition of a polypeptide shows a drastic change in its properties such as hydrophilicity and flexibility. This drastic change in its properties often plays an important role in life.

There are many kinds of synthetic polymers which respond to environmental conditions. For example, poly(*N*-isopropylacrylamide) shows a phase transition with temperature (LCST).[3] Such polymers vary their characteristics such as solubility and conformation with changing surrounding conditions such as temperature,[4] solvent composition,[5] pH,[5b,6] ionic strength,[5b,7] and electric field.[8] However, there are only a few reports of polymers which can vary their stiffness in response to environmental conditions like the polypeptide. If the stiffness of a polymer can be controlled by certain stimuli, numerous applications of the polymer will become possible.

We have already reported that poly(silamine), which consists of alternating 3,3-dimethyl-3-silapentane and *N,N'*-diethylethylenediamine units in the main chain, shows unique phase transition properties in response to the degree of protonation of amino groups in the poly(silamine) in aqueous media.[9] In the course of the studies on the phase transition properties of poly(silamine), it was found that poly(silamine) shows a strong interaction with several anions. Due to the interaction between poly(silamine) and anions along with the protonations of amino groups in poly(silamine), it was found that the rubber elasticity of poly(silamine) was drastically changed. This paper reports the elastic transition of poly(silamine) caused by the ion interactions.



Due to the presence of ethylenedimaine units in the main chain, poly(silamine) showed two-step deprotonation processes with changing pH values as follows:[10]



It was interesting to note that the p*K* values of poly(silamine) were influenced by the protonating agents. For example, the p$K_1$ value, which corresponds to $\alpha$ = 0.75, of poly(silamine) protonated by HCl was 5.8, while that by $H_2SO_4$ was 6.7, though their p$K_2$ values, which correspond to $\alpha$ = 0.25, were almost the same (Figure 1). This indicates that poly(silamine) has a special interaction with anions, *viz.*, $Cl^-$ and $SO_4^{2-}$, especially at an $\alpha$ of more than 0.5.

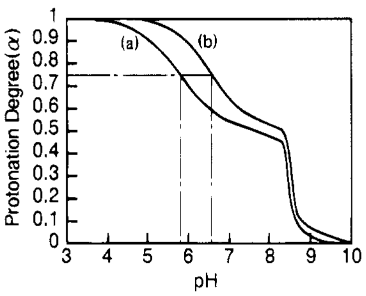


**Figure 1.** Plots of protonation degree ($\alpha$) of a solution of poly(silamine) versus pH of the solution at 25 °C. Protonating agent: HCl (a) and $H_2SO_4$ (b) (molecular weight of poly(silamine) = 2600).

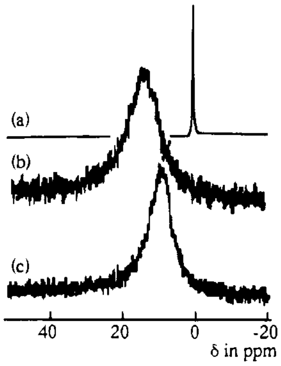


**Figure 2.** $^{35}Cl$ NMR spectra of a KCl aqueous solution (1.0 M KCl in $D_2O$) (a) and a poly(silamine) aqueous solution at $\alpha$ = 1.0 protonated by HCl ([N atom in poly(silamine)] = 0.5 M; [$Cl^-$] = 0.5 M) in the absence of $Na_2SO_4$ (b) and in the presence of $Na_2SO_4$ ([$Na_2SO_4$] = 0.25 M) (c).

Jhon and his co-workers reported that the binding forces between poly(vinylpyrrolidone) (PVP) and several anions can be estimated by NMR spectroscopy.[11] To obtain information about the interaction between poly(silamine) and the anions, $^{35}Cl$ NMR analyses were carried out according to Jhon's methodology. Contrary to the sharp $^{35}Cl$ signal of the KCl aqueous solution, as shown in Figure 2a, the signal of $^{35}Cl$ in a poly(silamine) aqueous solution ($\alpha$ = 1.0) protonated by HCl was very broad and shifted to a higher frequency field (Figure 2b). The broadened signal denotes a shortened transverse relaxation time (*T*2) due to the restricted mobility of the chlorine anion. The shortened *T*2 along with the chemical shift to the upper frequency field strongly indicated an interaction between poly(silamine) and the $Cl^-$ anion. When the same measurement was carried out in the presence of $SO_4^{2-}$ anions, the $^{35}Cl$ signal became narrower and shifted to the lower frequency field, as compared with that in the absence of $SO_4^{2-}$ anions (Figure 2c), indicating that the replacement of $Cl^-$ anions by $SO_4^{2-}$ anions took place due to the difference in coordination ability. As a result, $Cl^-$ anions became freer than in the absence of the $SO_4^{2-}$ anions due to the competitive bindings. Actually, the binding constants of the $Cl^-$ and $SO_4^{2-}$ anions toward poly(silamine) ($k_B$) were 0.91 and 1.46, respectively, which were determined using the equation reported by Jhon et al.

Contrary to the fact that the interaction between PVP and several anions in aqueous media increased with their decreasing lyotropic series,[11] poly(silamine) was

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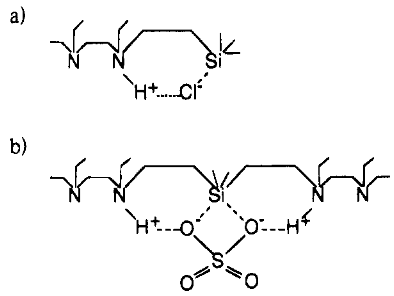

**Figure 3.** Possible poly(silamine) interactions with the $Cl^-$ anion (a) and $SO_4^{2-}$ anion (b).

bound more strongly to the $SO_4^{2-}$ anion than to $Cl^-$, indicating that the interaction of poly(silamine) with anions is governed not only by the Donnan equilibrium but also by the special interaction between poly(silamine) and anions. Since the Si atom shows weak Lewis acidity, the silicon atom in poly(silamine) plays an important role in the interaction with anions. Actually, a polyamine without a Si moiety shows a much lower p$K_1$ value (p$K_1$ = 5.0 at 23 °C[12]) than that of poly(silamine). We would like to propose the binding structures of poly(silamine) with $Cl^-$ and $SO_4^{2-}$ anions, as shown in Figure 3. In the case of the protonation by HCl, the Si atom interacts with $Cl^-$ to form a stable six-membered structure, which stabilizes the proton at the nitrogen atom. The strong interaction of poly(silamine) with the $SO_4^{2-}$ anion, contrary to the lyotropic series by Jhon, may be explained by the double chelating structure shown in Figure 3b.

It was reported that the rotation of amino groups around an ethylene bond axis is suppressed by their protonations.[13] Two of our authors (K.K. and T.T.) and their co-workers reported that the polyamine telechelic oligomer, which possesses ethylenediamine repeating units in the main chain, showed a stiffness change in the polymer by the protonation due to the rotation hindrance around protonated ethylenediamine units.[14] Since poly(silamine) possesses 3-silapentane and ethylenediamine alternative repeating units, flexibility of the polymer is very high. Actually, a glass transition temperature of poly(silamine) without protonation was −85 °C, which was one of the most flexible polymers known and is similar to silicone. As previously stated, the protonation of poly(silamine) at an $\alpha$ more than 0.5 accompanies the anion bindings. If our proposed binding is formed, the stiffness of the poly(silamine) in the highly protonated region must be significantly increased.

To obtain information on the stiffness change as a function of the protonation degree, DSC measurements of poly(silamine) with different degrees of protonation were carried out. Figure 4 shows the change in the glass transition temperature of poly(silamine) as a function of its degree of protonation. At a degree of dissociation of 0.5, the solid material undergoes almost a phase inversion. At lower ionization, the ionic groups are isolated[15] and the continuous mass of the film is the nonionized low-$T_g$ soft material. However, when the ionic groups dominate the composition, the polymer has the high $T_g$ expected from an ionomer. It should be noted that the $T_g$ of the poly(silamine) protonated by sulfuric acid was much higher than that of hydrochloric acid protonation, which may be explained not only by the ionization effect but also by the double chelating structure shown in Figure 3b. At $\alpha$ = 1.0 by sulfuric acid, the $T_g$ of the polymer became ca. 80 °C, which is comparable to that of polystyrene.

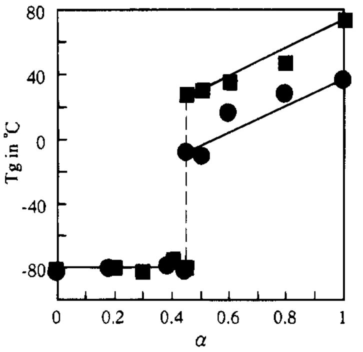

**Figure 4.** Change in the glass transition temperature of poly(silamine) as a function of the degree of protonation ($\alpha$). Protonating agent: HCl (●); $H_2SO_4$ (■). The glass transition temperatures were determined by DSC measurements of the sample prepared by freeze-drying of the poly(silamine) solutions after adjusting the pH to an appropriate value.

On the basis of these results, it was concluded that the rubber elastic transition of poly(silamine) is induced by the anion bindings along with the protonations. Especially, the change in the $T_g$ was more than 160 deg by the sulfuric acid protonation. Since the end groups of the poly(silamine) can be easily controlled, as previously reported,[9,16] poly(silamine) is promising not only as a new hydrogel but also as a novel stimuli-sensitive material such as hetero-cross-linkers and surface modification agents.

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## References and Notes

(1) Lehninger, A. L. *Biochemistry*, 2nd ed.; Worth Publishers: New York, 1977.
(2) Poland, D.; Scheraga, H. A. *Theory of Helix-Coil Transitions in Biopolymers*; Academic Press: New York, 1970.
(3) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2I*, 1441.
(4) (a) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820. (b) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163. (c) Katayama, S.; Hirokawa, Y.; Tanaka, T. *Macromolecules* **1984**, *17*, 2641. (d) Hoffman, A. S.; Afrassiabi, A.; Dong, L. C. *J. Controlled Release* **1986**, *4*, 213.
(5) (a) Hrouz, J.; Ilavsky, M.; Ulbrich, K.; Kopecek, J. *Eur. Polym. J.* **1981**, *17*, 361. (b) Ohmine, I.; Tanaka, T. *J. Chem. Phys.* **1982**, *77*, 5725.
(6) (a) Tanaka, T.; Fillmore, D. J.; Sun, S.-T.; Nishio, I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*, 1636. (b) Siegel, R. A.; Firestone, B. A. *Macromolecules* **1988**, *21*, 3254. (c) Batich, C. D.; Yan, J.; Bucaria, C., Jr.; Elsabee, M. *Macromolecules* **1993**, *26*, 4675.
(7) (a) Ricka, J.; Tanaka, T. *Macromolecules* **1985**, *18*, 83. (b) Park, T. G.; Hoffman, A. S. *Macromolecules* **1993**, *26*, 5045.
(8) (a) Tanaka, T.; Nishio, I.; Sun, S.-T.; Ueno-Nishio, S. *Science* **1982**, *218*, 467. (b) Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. *J. Appl. Polym. Sci.* **1992**, *46*, 635.
(9) Nagasaki, Y.; Honzawa, E.; Kato, M.; Kataoka, K.; Tsuruta, T. *Macromolecules* **1994**, *27*, 4848.
(10) Ogino, H. *Inorg. Chem.* **1980**, *19*, 1619.
(11) Song, J. D.; Ryoo, R.; Jhon, M. S. *Macromolecules* **1991**, *24*, 1727.
(12) Kikuchi, A.; Kataoka, K.; Tsuruta, T. *J. Biomater. Sci., Polym. Ed.* **1994**, *5*, 1994.
(13) Kazerouni, M. R.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1994**, *116*, 5279.
(14) Kataoka, K.; Koyo, H.; Tsuruta, T. *Macromolecules* **1995**, *28*, 3336.
(15) Lundberg, R. D. Ionic Polymers. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley: New York, 1987; Vol. 8, pp 393−423.
(16) Nagasaki, Y. Silicon-containing Monomers and Polymers. In *Functional Polymers for Emerging Technologies*; Arshady, R., Ed. (to be published).

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