

Friction of Gels. 7. Observation of Static Friction between Like-Charged Gels

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An extensive static friction has been observed when two like-charged polyelectrolyte gels are slid over each other in water. The two like-charged gel surfaces could not slip with each other at the initial shearing until the shear stress acting on the interface exceeded a certain critical value. The critical yield shear stress (static friction) and strain did not show a distinct dependence on the shearing rate but decreased with increasing temperature. The value of the static friction also increased with the increase in the normal pressure and effect of pressure becomes more substantial at a higher temperature. Furthermore, the static friction decreased 3–4 times when the counterions of the polyelectrolyte gels were changed from Na⁺ to Cs⁺. The observation of the static friction indicates that our previously proposed repulsion–adsorption model, which predicts a hydrodynamic mechanism with no static friction for two like-charged hydrogels in pure water, requires modification. Possible origins of the static friction are discussed.

1. Introduction

In the preceding papers,^{1–6} we have reported that hydrogels show a wide range of frictional forces when slid against themselves or on solid substrates. The gel friction coefficient μ , which is defined as the ratio between the frictional force (shear stress) to the normal load (compressive stress), changes over several orders from 10^{−3} to 10¹ depending on the combination of gels with different chemical structures. The extremely low value of the frictional coefficient of gels cannot simply be explained in terms of a hydrodynamic lubrication mechanism from a viewpoint of solid materials since it is sustained even at a Sommerfeld number as low as 10^{−11}, where the hydrodynamic lubrication can usually never be realized for friction between two solid surfaces.^{7,8}

To describe the specific behaviors of a gel friction when slid on a solid surface, we have proposed a thermodynamic model from the viewpoint of polymer–solid interface interaction (repulsion–adsorption model).² The main argument of this model is summarized as follows: In analogy to a polymer solution placed in contact with a solid wall, the polymer network on the gel surface will be repelled from (or adsorbed to) the solid surface if interface interaction is repulsive (or attractive). In the repulsive case, the solvent layer will be formed at gel–solid interface, so its viscous flow will make a dominant contribution to the friction. In the attractive case, however, the adsorbing polymer chain will be stretched when the solid surface makes a motion relative to the gel. The elastic force increases with the deformation and eventually the adsorbing polymer network detaches from the substrate, which in turn appears as the friction force. The theoretical analysis predicted that the attraction results in a high friction force with weak load dependence and the repulsion bring about a low friction force with a strong load dependence.² These predictions coincided with the experimental observations in a wide range of experimental conditions.^{3,4}

As a most typical repulsive case, dynamic friction between two like-charged hydrogels in pure water were studied theoreti-

cally and experimentally.⁴ When two like-charged hydrogels approach each other in water, an electric double layer is formed at the interface, and the friction arises from the hydrodynamic lubrication of the water layer. Assuming that the gel surfaces are homogeneously and continuously charged, the electrostatic potential distribution $\psi(z)$ between two charged surfaces in water can be obtained by solving the Poisson–Boltzmann (PB) theory⁴

$$e\psi(z)/kT = 2 \ln \cos(z\sqrt{n_0 r_0}/2) \quad (1)$$

Here z is the axis vertical to the gel surfaces with its origin at the symmetric plane, n_0 is the number charge density at the symmetric plane ($z = 0$), k is the Boltzmann constant, and T is the absolute temperature. $r_0 = e^2/\epsilon_r\epsilon_0 kT$ is a constant with a dimension of length (e , elementary electric charge; ϵ_r , relative dielectric constant of water; ϵ_0 , dielectric constant in a vacuum). The electric double layer thickness, $2l$, can be determined by the balance between the normal pressure applied to the gels, P , and the repulsion at the interfaces⁴

$$2l = 2\sqrt{2kT/Pr_0} \arctan(\sigma_e \sqrt{kTr_0/2P}) \quad (2)$$

Here, σ_e is the surface average charge number of the gels. The dynamic friction force, originated from viscous drag of water of the electric double layer, is

$$f = \frac{\eta v}{2(l + \xi)} \quad (3)$$

where η is the viscosity of water, v the sliding velocity, and ξ the network size of the gel. The appearance of ξ in eq 3 is associated with the permeability of the gel to water.⁴ Equations 2 and 3 predict that friction will increase with an increase in load and decrease with an increase in surface charge density of the gels. These predictions were semiquantitatively in agreement with experimental observations when the sliding velocity is not very low. However, we found that the friction force is almost not dependent on the velocity when both the sliding velocity and the load are low.⁶ This suggests that the hydrodynamic lubrication mechanism cannot describe comprehensively the

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friction behavior of the hydrogel. The specific hydration of water molecules, the counterion–polymer network interaction, and the rheological response of polymer chain might play important roles in polyelectrolyte gel friction.

The hydrodynamic interpretation predicts that no static friction should exist between two like-charged gels. To elucidate the validity of the prediction, we investigated the behaviors of the static friction between two negatively charged polyelectrolyte gels in water.

2. Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (Tokyo Kasei Co., Ltd.) was used as received and neutralized with sodium hydroxide (Junsei Chemical Co., Ltd.) in order to obtain the sodium salt of AMPS (NaAMPS). The cesium salt of AMPS (CsAMPS) was obtained with the same method as that of NaAMPS. *N,N'*-Methylenebis(acrylamide) (MBAA) (Tokyo Kasei Co., Ltd.) used as a cross-linking agent was recrystallized from ethanol. 2-Oxoglutaric acid (Wako Pure Chemical Industries, Ltd.), which was used as an UV initiator, was used as received.

Gel Preparation. Chemically cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid sodium salt) (PNaAMPS) gels were prepared by a radical polymerization of a 1.0 M aqueous NaAMPS monomer solution in the presence of 6.0 mol % MBAA and 0.1 mol % 2-oxoglutaric acid. The cross-linking polymerization was carried out by an UV ray irradiation for 5 h under a nitrogen atmosphere at room temperature. The reaction was carried out between two parallel glass plates separated by a silicone spacer 1 mm thick to give sheet-shaped gel. After gelation, gels were immersed in a large amount of pure water for 1 week to equilibrate swelling and wash away the residual chemicals. The degree of swelling of the gel, q , which is defined as the weight ratio of swollen to dry sample, was $q = 27$. The surface number charge density of PNaAMPS gel was $\sigma_e = 0.21 \text{ nm}^{-2}$.

Poly(AMPS cesium salt) (PCsAMPS) gel was synthesized in the same way as that of PNaAMPS gel with 4.8 mol % MBAA. The as-prepared PCsAMPS gel had $q = 28$ and $\sigma_e = 0.16 \text{ nm}^{-2}$.

Measurements. The friction between two PNaAMPS gels was performed using a commercially available rheometer (ARES, Rheometric Scientific Inc.) that works in a constant compressive strain mode. The swollen PNaAMPS gel, ca. 2 mm in thickness, was cut into a disk-shape of 15 mm in diameter and was glued on the upper surface of coaxial disk-shaped platen with cyanoacrylate instant adhesive agent (Toa Gosei Co., Ltd.). Another piece of PNaAMPS gel, which was also cut into a disk-shape of 25 mm in diameter, was glued onto the lower platen. The separated gel–gel interface was immersed in pure water at a prescribed temperature and equilibrated, and then the two specimens were allowed to approach with each other at a velocity of $2 \mu\text{m/s}$ until the normal load increased to a prescribed value.

To avoid the normal stress relaxation, measurements were performed after the normal strain was applied for at least 3 h, whereupon the normal stress reached a quasi equilibrium state. After the normal force stress-relaxation equilibrium was achieved, an angular displacement was applied to the lower platen at a constant angular velocity.

The frictional force, F , is calculated as $F = 4M/3R$, where M is the frictional torque recorded in measurement and R ($=7.5 \text{ mm}$) is the radius of the apparent contact area. The average

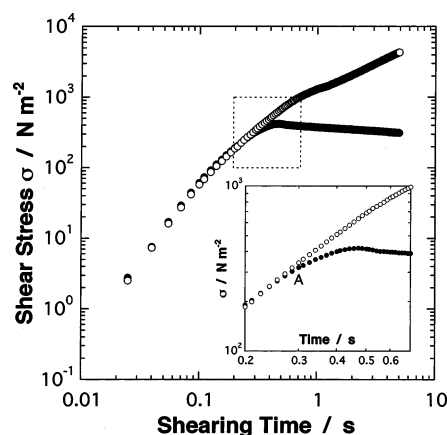


Figure 1. Frictional (●) and torsional (○) shear stresses as a function of shearing time measured in water at 20 °C. Inset: the enlarged view of the dotted square area to show the deviation of the frictional shear from the torsional shear in detail. Normal pressure: 14 kPa. Angular velocity: 10^{-2} rad/s .

frictional shear stress, σ , generated at the interface can be qualified as the friction force per unit area, that is, $\sigma = F/\pi R^2$. Details of the measurement were described in refs 4 and 6.

3. Results and Discussion

Figure 1 shows the time profile of the frictional shear stress when two PNaAMPS gels are rotated relatively at an angular velocity of 10^{-2} rad/s in water at 20 °C. As shown in the figure, the friction force increases rapidly with time at the beginning, reaches a peak in 0.4–0.5 s and then decreases gradually.

To know the point at which a true sliding phenomenon occurs at the interface, the two PNaAMPS gel surfaces were totally glued together using adhesive agent, and the shear was applied in a similar manner as the friction measurement. In this case, the detected torque is due to a torsional deformation of the gels behaving as one continuous body. As shown in Figure 1, the frictional and torsional shear stresses overlap with each other exactly until the frictional σ reached a peak value (to be exact, the frictional stress begins to deviate from the torsional one at point A).

This result informs us of an indisputable fact that the two like-charged gel surfaces, which are compressed under a normal pressure, cannot slip with each other until the shear stress acting on the interface exceeds a certain critical value, as if the two surfaces are glued together. This means that the frictional σ observed before the peak should be attributed not to a hydrodynamic viscous friction but to an elastic deformation of the polymer network by the torsion.

The deviation of point A to the peak value of the frictional force should be related to the disk-shaped sample, which gives a velocity distribution on the radial direction. For the simplicity, we adopt the peak value of the frictional shear stress as the critical shear stress σ_c that is required to slide the interface. On the other hand, the critical shear strain, γ_c , is defined in this study as

$$\gamma_c (\%) = \frac{R\omega t_c}{h} \times 100 \quad (4)$$

where R is the radius of the contact area, ω is the angular velocity, h is the total thickness of two compressed gels, and t_c is the critical time for the frictional stress to reach the maximum. For the present measurement, $\sigma_c = 420 \text{ N/m}^2$ and $\gamma_c = 0.93\%$ ($t_c = 0.46 \text{ s}$, $h = 3.7 \text{ mm}$). This static friction (σ_c) is ca. 10

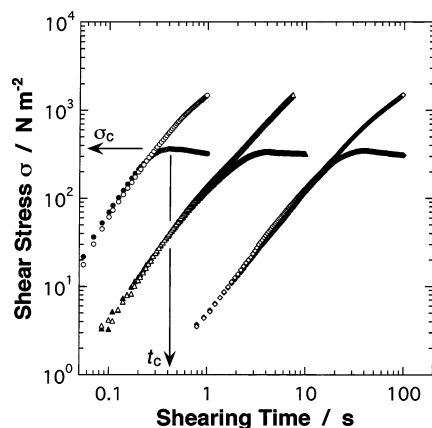


Figure 2. Time profiles of the frictional (solid symbols) and torsional (open symbols) shear stresses at various angular velocities in water at 20 °C. Normal pressure: 14 kPa. Angular velocity: 10^{-2} rad/s (●, ○); 10^{-3} rad/s (▲, △); 10^{-4} rad/s (◆, ◇).

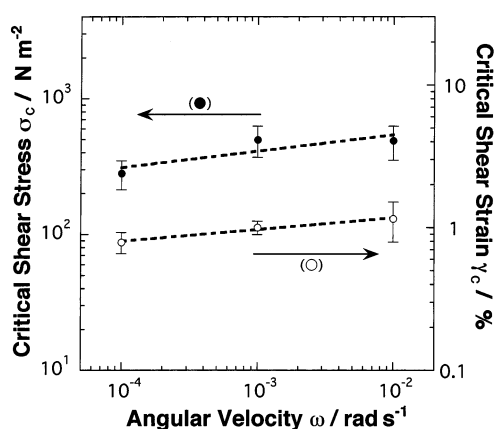


Figure 3. Angular velocity dependences of the critical shear stress (●) and critical shear strain (○) as determined from the peaks of the frictional shear stresses. The error ranges in the figure are standard deviations of the mean values over three samples. Normal pressure: 14 kPa. Temperature: 20 °C.

times larger than the dynamically equilibrated value measured at the same normal pressure and angular velocity.⁶ Nevertheless, it should be emphasized that the value of σ_c is not so large considering the normal pressure of 14 kN/m². The ratio of σ_c to the normal pressure, i.e., the maximum static friction coefficient, is 0.03, which is still much lower than that of solid friction.

To study whether this static friction depends on the shear rate or not, we have measured the friction under various angular velocities. The similar results (i.e., frictional σ = torsional σ before the appearance of the frictional peak value) are also observed at angular velocities of 10^{-3} and 10^{-4} rad/s, as shown in Figure 2. Considering the peak point of the frictional shear stress as the critical point, the critical shear stress σ_c and strain γ_c are shown as a function of the shearing velocity in Figure 3. σ_c and γ_c are almost independent of the shearing velocity over 2 orders of magnitude. This result indicates that two like-charged gel surfaces do not slip with each other regardless of the angular velocity in a range of 1×10^{-4} to 1×10^{-2} rad/s until the shear strain reaches a critical value of γ_c . In other words, the interface behaves like “adhered”, showing an elastic–plastic transition despite the electrostatic repulsive interaction between two gel surfaces.

Therefore, the observed static friction suggests the existence of a certain attractive interaction between the two gel surfaces despite of their repulsive interface nature.

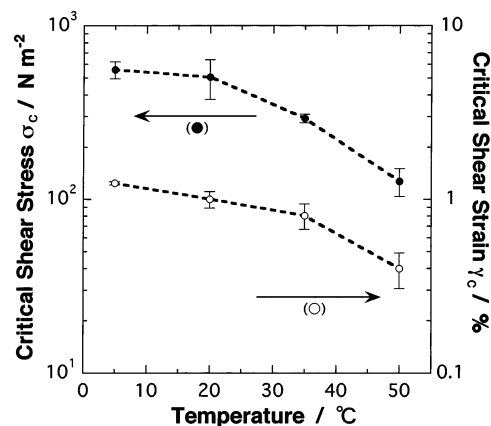


Figure 4. Temperature dependences of the critical shear stress (●) and strain (○). The error ranges in the figure are standard deviations of the mean values over 3 samples. Normal pressure: 14 kPa. Angular velocity: 10^{-3} rad/s.

One intuitive possibility for the origin of the static friction is the surface roughness effect. Sliding between two surfaces with a finite roughness might give a static friction due to entrapment of compensative part of the surfaces.

To clarify this possibility, σ_c and γ_c were measured as a function of temperature. Here, one should notice that increasing the temperature would bring about two effects. One is an increase in the elastic modulus of polymer network. For example, when the temperature is raised from 5 to 50 °C, the elastic modulus change of an ideal polymer network is $(273 + 50)/(273 + 5) = 1.16$ times. In fact, our previous work has shown that the elastic modulus of the PNaAMPS gel increases 1.11 times when temperature changes from 5 to 50 °C.⁶ This increase in the elastic modulus would result in an increase in σ_c if the static friction has a topological origin. Another effect of increasing temperature is to bring about a decrease in the viscosity of water. When the temperature is raised from 5 to 50 °C, the viscosity of bulk water decreases $\eta(50\text{ °C})/\eta(5\text{ °C}) = 1/2.8$ times. A similar temperature effect is expected to waters inside the gels as well as on their surfaces.

Figure 4 shows the temperature dependences of σ_c and γ_c obtained at an angular velocity of 1×10^{-3} rad/s. As shown in the figure, both σ_c and γ_c decreased substantially with increasing in temperature. When the temperature is raised from 5 to 50 °C, the change in the critical shear stress is $\sigma_c(50\text{ °C})/\sigma_c(5\text{ °C}) = 1/4.4$ times, as obtained from Figure 4. This result indicates that the static friction associated with the topological origin, the surface roughness, can be excluded. Taking account of the soft nature of the polymer network (the dynamic elastic modulus of this gel is 0.13 MPa⁶), this is quite understandable because the gel surfaces should be self-adjustable to avoid a local high electrostatic repulsion brought about by surface roughness. In fact, the dynamic sliding friction showed no distinct dependence on the surface roughness of the gel.⁹

Furthermore, it is found that the critical shear stress (static friction) increases with the increase in the normal pressure P but the effect of pressure is depended strongly on the temperature, as shown in Figure 5. If $\sigma_c(28\text{ kPa})/\sigma_c(14\text{ kPa})$ is plotted against the temperature T , we get a linear relationship between them, which indicates that the effect of normal pressure increases with the increase in temperature (Figure 5 insert).

The temperature dependences of the static friction shown in Figures 4 and 5 suggest that the state of water is important in the appearance of static friction. Recent studies on water confined between two mica surfaces have demonstrated a

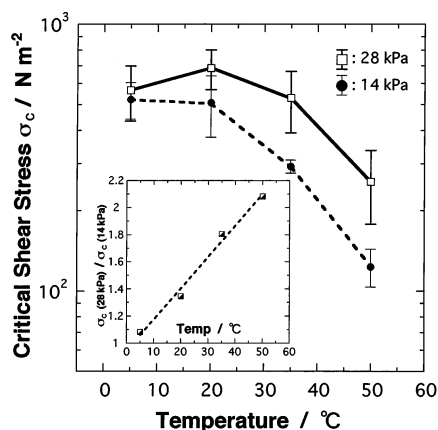


Figure 5. Relationship between critical shear stress and temperature under a low (14 kPa) (●) and a high (28 kPa) (□) normal pressure. The error ranges in the figure are standard deviations of the mean values over three samples. Angular velocity: 10^{-3} rad/s. Insert is a figure showing the temperature dependence of the ratio of the critical stress at 28 kPa to that at 14 kPa.

solidlike transition of water molecules when they were confined in a gap several angstrom in thickness. If the confined thickness becomes larger, the effective viscosity of water decreases to the value comparable to the bulk one.¹⁰ To compare with this result, the thickness of the electric double layer was calculated using eq 2, and it is estimated as 22.8 and 15.7 nm at 20 °C for $P = 14$ and 28 kPa, respectively. These values are much larger than the critical water-layer thickness to cause a solid–liquid transition between mica surfaces.

In the electric double layer formed between two charged gel surfaces, water molecules are strongly hydrated to the counterions (Na^+) of the polymer network, and this strong hydration should influence substantially the interaction between the counterions and the charged network. There have been observed several unique facts suggesting the presence of strongly hydrated water apart from the bulk water in a highly charged network. For instance, a weakly cross-linked PNaAMPS gel can swell as much as 3000 times of the dry network, and the gel still keeps its shape. This fact suggests that a long-range interaction of water molecules (submicrometers) with the polymer network may exist via counterions owing to their strong hydration ability. Not only in the network but also on the network surface, the water molecules are considered to be in a “bound” or “hydrated” state, and their properties are different from those of the bulk water.

Since the hydration is strongly dependent on the species of ions, we further studied the static friction σ_c between two PCsAMPS gels in water. The hydration ability of Cs^+ ions is smaller than that of Na^+ ions. As shown in Figure 6, PCsAMPS gel showed a 3–4 times smaller σ_c than that for the PNaAMPS gel. This result indicates that the hydrated state of the counterions do play an important role in the static friction. Then, what causes the static friction?

It was reported the appearance of counterion-mediated attraction between like-charged macromolecules, such as DNA, F-actin, etc.^{11,12} This effective attraction via counterions, however, appears only in the presence of multivalent counterions, which conflicts with our present system.

Kurihara et al. showed a density-dependent transition of polyelectrolyte chain:¹³ When the density of the chain grafted on mica surface exceeds over a criticality, its elastic modulus decreases drastically. This is explained in terms of the transition in the binding mode of the counterions to the polyelectrolytes, from the loosely bound state to the tightly bound one which

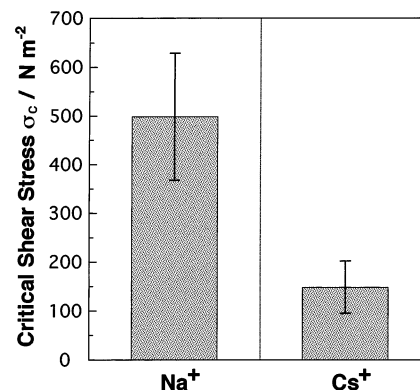


Figure 6. Dependence of the critical shear stress on the species of counterions. Normal pressure: 14 kPa. Angular velocity: 10^{-3} rad/s. Temperature: 20 °C.

reduces intra- and interchain repulsive interactions. If the same effect occurs in our experimental system when the osmotic repulsion at the constraint interface becomes thermodynamically unstable, the repulsive interface interaction decreases and van der Waals attraction becomes dominant, which might give a static friction. However in this case, the less the hydration ability, that is, the less the dissolubility of Cs^+ than Na^+ should lead to a larger static friction, which is not true (Figure 6).

We consider that a possible origin of the static friction might be due to the specific water structuring. As is well-known, the presence of Na^+ in water promotes the water structuring due to its high hydration ability, and the thermal fluctuation of water molecules is reduced. On the other hand, due to little hydration, Cs^+ ions destroy the hydrogen-bonding network of waters. This explains why $\sigma_c(\text{Na}^+)$ is larger than $\sigma_c(\text{Cs}^+)$, assuming that the static friction between like-charged gels originates from the specific water structuring at the interface.

Another possible origin of static friction is due to discrete surface charge effect. If the distance between two gel surfaces is comparable to the polymer mesh size, the discrete charge distribution on the polymer mesh becomes important. In this case, the electrostatic potential as well as counterion distribution varies along the direction parallel to the gel surface. When a shear force is applied to make a sliding, the electrostatic force would appear in such a way to resist the sliding since the change in position along the gel surface would change the electrostatic energy of the system. In other words, the counterions are forced to change their distributions from the thermally equilibrated state by the shear force. This induces an attraction of the compensative network charges on gel surfaces to the counterions to pull them back to the original equilibrated state. As a result, two repulsive gel surfaces would attract with each other via their counterions and show a static friction.

4. Conclusions

We found, for the first time, that the like-charged gel interface could not slip with each other until the shear stress (strain) overcame a criticality. The critical value of the shear stress (static friction) is ca. 10 times higher than that of the dynamic frictional force, almost independent to the shearing rates, decreases with increasing in temperature, and increases with increase in the normal pressure. The static friction is also dependent on the species of counterions of the polyelectrolyte gels. These results indicate that the friction between two like-charged polyelectrolyte gels could not interpreted by the hydrodynamic lubrication between two parallel surfaces mediated by pure water. The electrostatic interaction between counterions and the charged

network might be the origin of the static friction, whereupon the hydration of water to the counterions plays an important role, and more systematic study is necessary in the future in order to elucidate the nature of the static friction.

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References and Notes

- (1) Gong, J. P.; Higa, M.; Iwasaki, Y.; Katsuyama, Y.; Osada, Y. *J. Phys. Chem. B* **1997**, *101*, 5487.
- (2) Gong, J. P.; Osada, Y. *J. Chem. Phys.* **1998**, *109*, 8062.
- (3) Gong, J. P.; Iwasaki, Y.; Osada, Y.; Kurihara, K.; Hamai, Y. *J. Phys. Chem. B* **1999**, *103*, 6001.
- (4) Gong, J. P.; Kagata, G.; Osada, Y. *J. Phys. Chem. B* **1999**, *103*, 6007.
- (5) Gong, J. P.; Iwasaki, Y.; Osada, Y. *J. Phys. Chem. B* **2000**, *104*, 3423.
- (6) Kagata, G.; Gong, J. P.; Osada, Y. *J. Phys. Chem. B* **2002**, *106*, 4596.
- (7) Persson, B. N. J. *Sliding Friction, Physical Principles and Applications*; Springer: Berlin, 1998.
- (8) Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley & Sons: New York, 1990.
- (9) Kurokawa, T.; Gong, J. P.; Osada, Y. *Macromolecules* **2002**, *35*, 8161.
- (10) Raviv, U.; Laurat, P.; Klein, J. *Nature (London)* **2001**, *413*, 51.
- (11) Bloomfield, V. A. *Biopolymers* **1991**, *31*, 1471.
- (12) Tang, J. X.; Wong, S.; Tran, P.; Janmey, P. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1.
- (13) Abe, T.; Higashi, N.; Niwa, M.; Kurihara, K. *Langmuir* **1999**, *15*, 7725.