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Synthesis of Hydrogels with Extremely Low Surface Friction

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Design and production of hydrogels with a low surface friction are crucially important in the biomedical applications of hydrogels as contact lens, catheter, artificial articular cartilage, artificial esophagus, etc. Great efforts to pursue suitable polymer systems have been made on designing and production of artificial organs with a sufficient lubrication.[1,2] We report here a method to prepare hydrogels with an extremely low surface friction.

Usually a hydrogel is synthesized in glassware or on a glass substrate, and it has a mirrorlike smooth surface. This is the same when a hydrogel is synthesized on other hydrophilic substrates such as mica and sapphire. Focusing on the smooth surface of the gels, we have made systematic studies on the surface sliding friction of gels,[3−5] and found that the frictional behavior of hydrogels does not conform to Amonton's law $F = \mu W$, which well describes the friction of solids. Instead, the frictional force is strongly dependent on the sliding velocity and the normal load. Hydrogels exhibit a wide range of frictional coefficients from an order of 10^{-3} to 10^{0} in magnitude, depending on the interfacial interaction between the polymer network and the opposing substrate. When the interfacial interaction is attractive, the force to detach the adsorbing chain from the substrate appears as friction to give a high frictional coefficient. When the interfacial interaction is repulsive, a water layer is retained at the interface even under large normal loads, to give a very low frictional coefficient.[3,4] Polyanionic gels, for example, exhibit frictional coefficients in an order of 10^{-2} when slide on a piece of glass substrate in pure water due to the electrostatic repulsion between the gel and the glass.[5]

However, we discovered recently that, even for the same chemical structure, a hydrogel exhibits a much lower surface friction when it is synthesized on a hydrophobic substrate such as polytetrafluoreoethylene (Teflon) and polystyrene (PS). The differences in the surface nature of the gels synthesized on different substrates are so obvious that they can be easily distinguished by touching with one's finger.

The poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) gel was synthesized by the radical polymerization. An aqueous solution of 1.0 M 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), 5.0 mol % cross-linking agent, *N*,*N*′-methylenebisacrylamide(MBAA), and 0.1 mol % initiator, 2-oxoglutaric acid, in the reaction cell was purged with nitrogen gas for 30−45 min and was irradiated with UV light for 5 h at 20 °C. The reaction was carried out between a pair of polystyrene substrates or glass substrates, separated with a spacer 2 mm thick. After polymerization, the gel was immersed in a large amount of water for 1 week to equilibrate and to wash away the residual chemicals. The swollen PAMPS gels (swelling degree $q = 21$ on glass and $q = 27$ on PS) were ca. 0.4 cm thick and they were cut into square shapes of 1.0 × 1.0 cm^2 for the friction measurement using a commercialized rheometer (3ARES-17A, Rheometric Scientific F. E. Ltd.) with a coaxial two parallel planar geometry. The gel was crapped on the upper surface of the platen and a glass plate was fixed at the lower platen of the rheometer. The torque and the normal force were detected when the lower platen rotated with an angular velocity at a strain-constant mode in water at 25 °C. The average frictional force was calculated from the torque. Details of the measurements were described in ref 5.

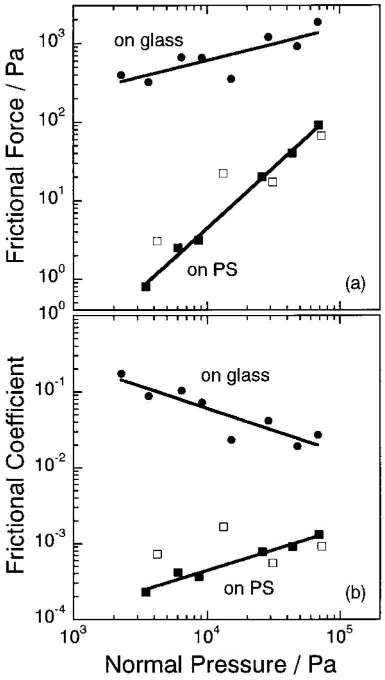

Figure 1. Normal pressure dependence of the frictional force (a) and the frictional coefficient (b) of PAMPS gels slid against a glass plate in water at an angular velocity of 0.01 rad/s: (●) prepared on glass, swelling degree, 21; (■) prepared on PS, swelling degree, 27; and (□) containing linear polymer chains, swelling degree, 15.

Figure 1 shows the normal load dependence of the frictional force (Figure 1a) and the frictional coefficient (Figure 1b) for PAMPS gel synthesized on a glass plate and on a PS plate. Figure 2 is the angular velocity dependence of the frictional coefficient for two gels. As shown in Figures 1 and 2, the frictional coefficient of the gel prepared on PS is at least two orders lower in magnitude than that of the gel synthesized on glass in the low pressure and the low velocity ranges, attaining a value as low as 10^{-4}. Our previous studies showed that the frictional force between two pieces of PAMPS gels in water only weakly increase with the decrease in the swelling degree of the gels,[5] therefore, the large difference observed here should not be attributed to the small difference in the water content or the ionic strength, but to the different surface nature of the gels.

Such a substrate effect is observed in a wide variety of hydrogels prepared from water-soluble vinyl monomers, such as the sodium salt of styrene sulfonate, acrylic acid, and acrlyamide, on various hydrophobic substrates, such as Teflon, polyethylene, polypropylene, poly(vinyl chloride), and polymethyl methylacrylate (PMMA).[6]

As has been reported in the preceding papers, when a hydrogel is prepared in water, the gelation on the hydrophobic substrate is suppressed to give a heterogeneous structure of the gel.[6,7] The suppression of the gelation on the hydrophobic surface brings

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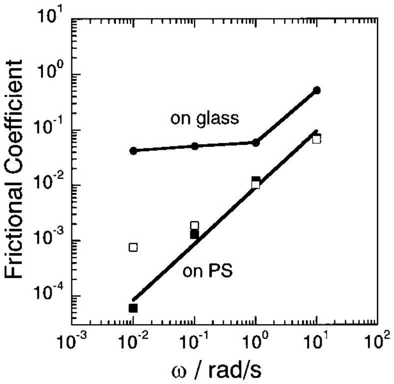

Figure 2. Angular velocity dependence of the frictional coefficient of PAMPS gels slid against a glass plate in water under a normal pressure of 4 × 10^3 Pa: (●) prepared on glass;, (■) prepared on PS; and (□) containing linear polymer chains.

about an extensive diffusion of monomers in the surface region to the adjacent region where the monomer has already been consumed and leads to a gradient network density. One can assume from this result that such a suppressed polymerization near the hydrophobic substrate cannot make an efficient cross-linking reaction, but leads to the formation of branched dangling polymer chains.

The lower cross-linking density of the gel close to the hydrophobic substrate is coincident with the fact that the surface layer synthesized on PS showed a lower compressive modulus of ~10^3 Pa while that in the bulk layer or the surface layer prepared on glass showed a value of ~10^4 Pa.[8]

To prove the inhomogeneity of the network, a diffusion experiment of bovine serum albumin (BSA) in the surface layer of two kinds of gels, one synthesized on the glass and the other on PMMA plate, was made by using Fluorescence Correlation Spectroscopy (FCS). BSA is an oval-shaped protein with a molecular dimension of 14 × 4 × 4 nm^3,[9] which is large enough to sensitively recognize the network size of the gel. Poly(styrene sulfonate sodium salt) (PNaSS) gels with various equilibrium swelling degrees were synthesized on a glass or a PMMA, and were washed in phosphate buffered solution (pH 7.4) before being immersed in Alexa Fluor 488-labeled BSA (A-BSA, Molecular Probes, Eugene, OR) (0.01 mg/mL) solution containing unlabeled BSA (10 mg/mL) overnight. FCS measurements were performed at 25 °C using a Fluorescence Correlation Measurement System (ConfoCor, Carl Zeiss Jena GmbH, Jena, Germany). Details were described in ref 10.

Figure 3 shows the diffusion constant, D, ca. 200 μm beneath the gel surface. As shown in Figure 3, D of BSA in the gel prepared on PMMA is much higher than that in the gel prepared on the glass and the former is the same value as that in the corresponding linear PNaSS solution. Since the D of BSA strongly depends on the cross-linking density of the gel, this result suggests that the gel surface synthesized on PMMA has branched dangling chains on the cross-linked network.

To elucidate the effect of branched dangling chains on friction, we additionally synthesized the PAMPS gels containing free PAMPS chains inside the network and studied its frictional behavior. The free chain containing gel was prepared as follows: An aqueous solution of 1.0 M AMPS, 8.0 mol % MBAA, and 0.1 mol % 2-oxoglutaric acid was polymerized between two glass plates under the conditions described in the previous section and then immersed in a 5.0 M AMPS monomer solution until reaching equilibrium. Next, the polymerization without the cross-linking agent was performed in the PAMPS gel. The gel thus prepared consists of the polymer network entangled with linear polymer chains. From the weight change in the dry gels before and after the second polymerization, the weight ratio of the network to the linear chains was found to be 4:6. By the same method, it was found that only <0.2% of the linear chains inside the gel diffused out after being immersed in water for 2 weeks. Therefore, the linear chains were effectively trapped in the gel network.

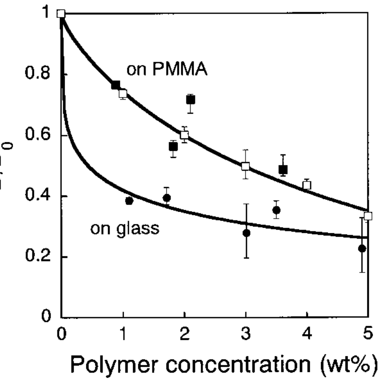

Figure 3. Polymer concentration dependence of the relative diffusion coefficient D/D_0 of BSA in the surface layers (ca. 200 μm beneath the surface) of PNaSS gels prepared on PMMA (■) and on glass (●). The relative diffusion coefficient of BSA in the PNaSS solution is also shown in the figure (□). D_0 is the diffusion coefficient of BSA in water.

The free polymer chains existing near the gel surface may exert a similar effect as that of branched dangling chains to reduce the friction. The results are shown in Figures 1 and 2, which show nearly the same behavior as those of the polymer gel prepared on PS substrate. Thus, incorporating linear polymers into the network, like the dangling chains, might bring about a substantial reduction in the friction coefficient.

The reduced frictional coefficients of the gel in the presence of the branched polymer chains might be associated with the enhanced hydrodynamic thickness of the solvent layer. As has been discussed in our previous work,[3-5] when the interfacial interaction is repulsive between gel and the substrate on which the gel is slid, a water layer is retained at the interface even under large normal loads to give a low friction. Under the same pressure, the static solvent layer thickness should be the same for both the chemically cross-linked gel and the gel having polymer brushes on its surface. However, under a shear flow, the polymer brushes are deformed more easily than that of the cross-linked network and this would increase the effective thickness of the hydrodynamic layer to reduce the shear resistance. Further study is needed to exploit the mechanism.

As far as we know, neither experimental results nor theoretical models accounting for the substantial reduction of the frictional force by the polymer brushes on the gel surface have been reported. This discovery may be useful in finding novel approaches in the design of low-friction artificial organs or even informative for understanding the efficient lubrication mechanism observed in biological systems.

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