Substrate Effect on Topographical, Elastic, and Frictional Properties of Hydrogels

T. Kurokawa,[†] J. P. Gong,*[,†,‡] and Y. Osada[†]

Graduate School of Science, Hokkaido University, and PRESTO, JST, Sapporo 060-0810 Japan

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ABSTRACT: Cross-linked poly(*N*,*N*′-dimethyl acrylamide) hydrogels were prepared on hydrophilic silicon substrates or hydrophobic polystyrene substrates and their topographical elastic properties were investigated by atomic force microscopy (AFM). The gels prepared on the hydrophobic substrate have a much rougher surface morphology with a lower surface elastic modulus than those prepared on the hydrophilic substrate. The topographical and mechanical properties of the gel have little influence on the surface friction, and the lower surface friction observed for the gel prepared on the hydrophobic substrate was attributed to the presence of dangling free polymer chains formed in the course of the polymerization.

1. Introduction

In our previous papers, it has been reported that hydrogels prepared by radical polymerization of aqueous vinyl monomer solutions on hydrophobic substrates exhibit not only increased swelling,[1] but also unique surface properties such as an extremely low friction coefficient[2] and decreased adhesion to cells.[3]

To elucidate the mechanism of these substrate effects two noninvasive techniques, electronic speckle pattern interferometry (ESPI)[4] and real time laser sheet refraction (RT-LSR),[5] were developed and used successfully to monitor the spatial and temporal profiles of polymerization and gelation. It was found that polymerization is extensively suppressed on the hydrophobic surface, leading to a gradient polymerization profile with a depth on the order of millimeters.[2,6] The gradient polymerization profile on the hydrophobic substrate is observed for a wide variety of vinyl monomers, such as 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and its sodium salt, the sodium salt of poly(styrenesulfonic acid), acrylic acid, acrylamide, and *N*,*N*′-dimethyl acrylamide (DMAAm). This kind of substrate effect was also confirmed on various hydrophobic substrates, such as Teflon, polyethylene, polypropylene, polystyrene (PS), and poly(vinyl chloride), but not on hydrophilic substrates, such as glass, sapphire, silicon, and mica. The lower the surface tension of the substrate, the larger was the observed gradient of gelation.[1,7]

The substrate effect was explained by the changes in the kinetic process, due to specific surface properties of the hydrophobic surface.[6] According to this interpretation, the rougher the surface and the lower the surface tension of the substrate, the more extensively does the substrate effect appear. The diffusion behavior of proteins in the surface region of the gel suggests that the surface region of the gel synthesized on a hydrophobic substrate consists of a loosely cross-linked network with many free dangling chains.[2] Microrheological investigations of PAAm gels showed that the local shear modulus decreased while the viscosity increased on approaching the substrate over a distance range of millimeters for gels made on Teflon.[8]

This paper reports, the surface topography and elastic modulus of gels prepared on hydrophilic and hydrophobic substrates were studied by atomic force microscopy (AFM). The influences of surface roughness and surface elasticity on the sliding friction are discussed by comparing the topographic images with the frictional results. The role of free polymer chain ends on the friction is investigated.

2. Experimental Section

2.1. Materials. *N*,*N*-Dimethylacrylamide (DMAAm) (Tokyo Kasei Co., Ltd.), was distilled at 30 °C. *N*,*N*′-Methylenebis-(acrylamide) (MBAA) (Tokyo Kasei Co., Ltd.), used as a cross-linking agent, was recrystallized from ethanol. 2-Oxoglutaric acid (Wako Junyaku Co., Ltd.), used as a radical initiator activated by UV light, was used without purification. Potassium persulfate (Tokyo Kasei Co., Ltd.) was recrystallized from water.

2.2. Gel Preparation. Gel samples were prepared between two parallel substrates separated with a spacer 2 mm in thickness. Poly(*N*,*N*-dimethylacrylamide) (PDMAAm) gels were prepared by radical polymerization of a 1.0 mol/L aqueous solution of DMAAm monomer in the presence of a 5 mol % MBAA and 0.1 mol % potassium persulfate. The PDMAAm polymerization was carried out at 60 °C for 7 h. PDMAAm gels containing linear polymer chains were prepared between a pair of mirror-polished silicon substrates in the 1.0 mol/L DMAAm monomer solution containing 0.1 mol % potassium persulfate. On attaining equilibrium, the gel was taken out and sandwiched between a pair of silicon substrates, and the polymerization was continued at 60 °C for 7 h.

2.3. Substrate Preparation. Mirrorlike polished silicon wafers were purchased from Shin-Etsu Chemical Co., and a silicon wafer with a rough surface was obtained courtesy of Ricoh Co.. Commercially available polystyrene was used as a hydrophobic substrate. All the substrates were washed carefully with detergent in a sonicator, and then rinsed with a large amount of distilled water.

2.4. Measurements. The surface roughness of substrates was characterized by AFM in tapping mode (Nano Scope III, Digital Instruments) in air. The surface scanning range was $20 \times 20\ \mu m^2$. R_q, the root-mean-square average of height deviations from the mean data plane, was estimated. R_q is defined by

$$R_q = \sqrt{\sum_{i=1}^{N} f(x_i)^2/\mathrm{N}} \qquad (1)$$

where $f(x_i)$ is the surface height at point x_i.

* Corresponding author. E-mail: gong@sci.hokudai.ac.jp. Telephone: 81(11)706-2774. Fax: 81(11)706-2635.
† Graduate School of Science, Hokkaido University.
‡ PRESTO, JST.

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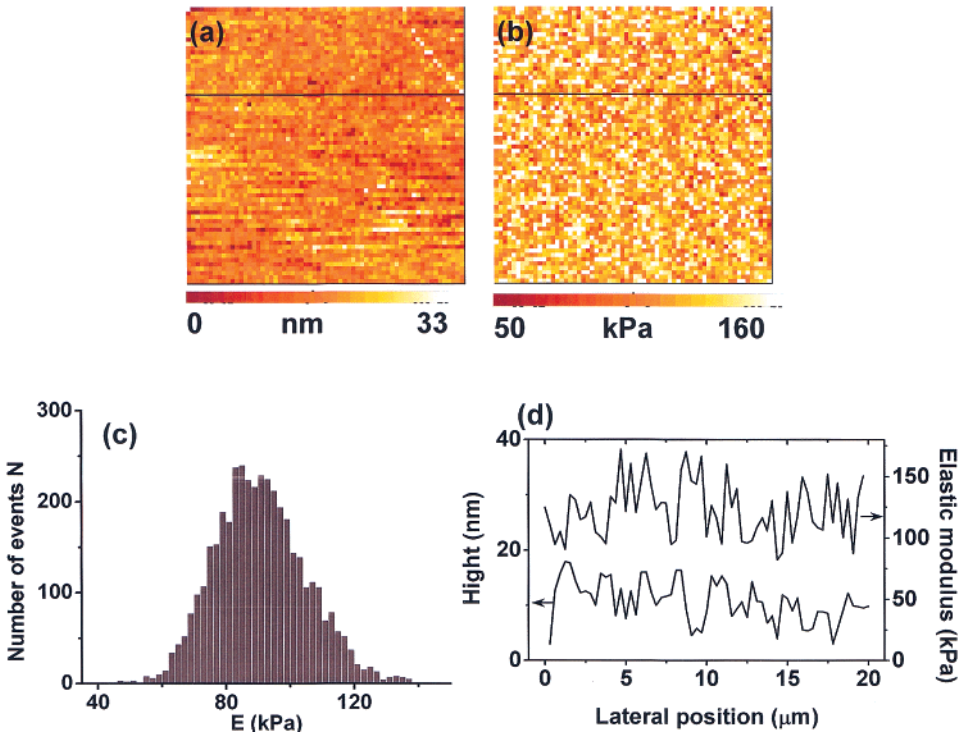

Figure 1. Topographical image (a), elastic modulus image (b), histogram of elastic modulus (c), and the height and modulus profiles (d) of a PDMAAm gel prepared on a silicon substrate. Data on the horizontal lines in parts a and b are plotted in part d. Scanning area: $20 \times 20\ \mu m^2$.

The topographical images and elastic modulus images of the hydrogels were obtained by using commercially available AFM equipment (SPI3800, Seiko Inc.) in water at 25 °C. A piezoelectric scanner with a maximum x, y scan range of $100 \times 100\ \mu m^2$ and a z range of 10 μm was used. Triangular cantilevers of Si_3N_4 (Park Scientific Instruments) with a tip angle of 70° were used, and the spring constants of the cantilevers were determined from their thermal fluctuations, with a typical value of 0.50 N/m. The 64 pixels × 64 lines force−displacement curves and topographic images of contact AFM mode were obtained simultaneously. Elastic moduli were obtained by analyzing force−distance curves using the Hertz model[9] that is for describing the elastic response of a soft sample indented by a stiff AFM tip. The offset of force is determined by calculating the mean force at the very beginning of the force curves, where the AFM tip is off the sample surface. The zero displacement point is determined by performing a Monte Carlo fit as follows:[10] Two displacement values with their corresponding force values are selected and substituted to the Hertz model. These two data points set up two equations that can be inverted to obtain values for the elastic modulus and the offset of the displacement. A Poisson ratio of 0.5 was used in the analysis. The force-displacement curves with advancing distances of ca. 0.1 and 3 μm were used to estimate the elastic modulus for gel prepared on the silicon substrate and on the PS substrate, respectively. Detailed experimental procedures were described in the literature.[10,11]

The images presented are representative of the entire surface of the gel. Surfaces with different scan areas of 5×5, 10×10, 20×20, 50×50, and $100 \times 100\ \mu m^2$ were investigated; to save space, images of $20 \times 20\ \mu m^2$ are presented. Topographical and modulus images shown are of the same surface region of the gel, and regions imaged were randomly selected. The histograms of moduli were determined from the images shown.

A commercially available rheometer "ARES" (advanced rheometric expansion system, Rheometric Scientific Inc.) was used for measuring the surface sliding friction of gels. Samples of 2.2 mm in thickness were cut into ring shapes (inside radius $r_i = 5$ mm; outside radius $r_o = 10$ mm) and were glued onto the upper surface of a coaxial disk-shaped platen. The same kind of gel was used as the opposing substrate. The substrates were slightly larger than the upper ring-shaped gel and were fixed onto the lower platen. The interface was immersed in water during the measurements. Prior to measurement, a certain amount of normal stress was loaded onto the gels for a minimum of 60 min, until they reached equilibrium. After achieving stress-relaxation equilibrium, an angular displacement with an angular velocity, ω, was applied to the lower platen to generate the frictional torque. The torque, T, as well as the normal stress were recorded during the rotation. The total frictional force, F, is calculated from

$$F = \frac{4(r_o^3 - r_i^3)}{3(r_o^4 - r_i^4)}T \qquad (2)$$

Detailed description of the friction measurements is as given in previous papers.[12,13]

3. Results and Discussions

Surface Morphology and Elasticity. Figure 1a and Figure 2a show the AFM topographic images of the PDMAAm gels synthesized on the silicon substrate and on the polystyrene substrate, respectively. The gel surface synthesized on the silicon substrate is extremely smooth, showing a root-mean-square average of height deviations, R_q, as small as 5.0 nm. On the other hand, R_q of the gel synthesized on the PS substrate is 140 nm, which is about 30 times larger than that synthesized on the silicon substrate. If we compare the topographical data of gels to their templates, which are shown in Table 1, it is found that the R_q value of the gel prepared on the silicon surface is about 5 times larger than that of the silicon substrate. However, R_q of the gel prepared on the PS is about 50 times larger than that of the PS substrate.

Figure 1b and Figure 2b show the corresponding elastic modulus images of PDMAAm gels prepared on the silicon substrate and the polystyrene substrate,

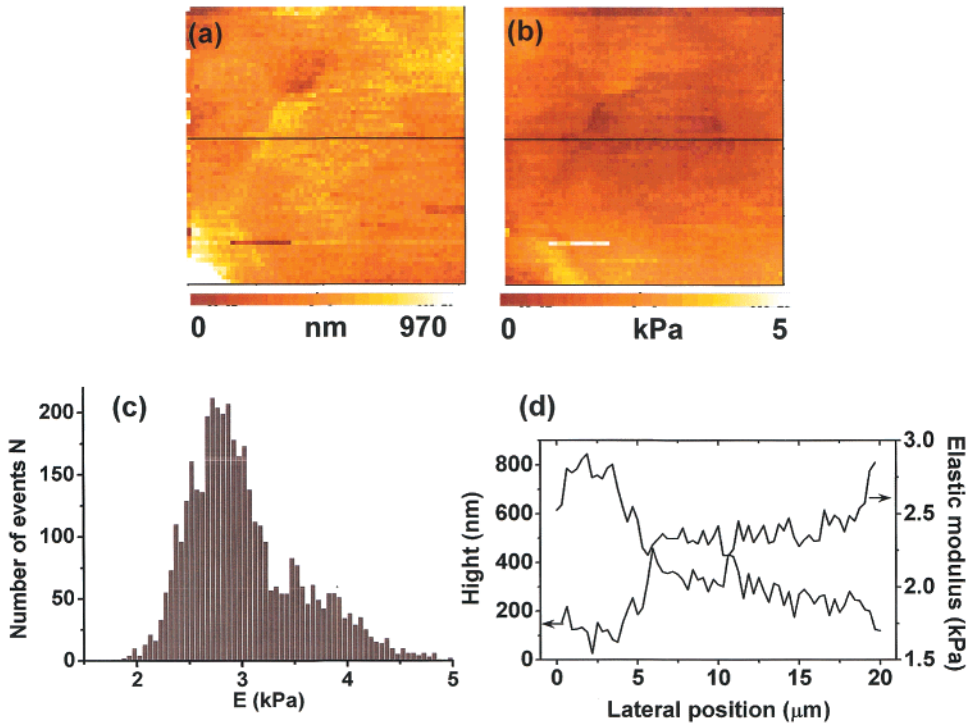

Figure 2. Topographical image (a), elastic modulus image (b), histogram of elastic modulus (c), and the height and modulus profiles (d) of a PDMAAm gel prepared on a polystyrene substrate. Data on the horizontal lines in parts a and b are plotted in part d. Scanning area: $20 \times 20\ \mu m^2$.

Table 1. Surface Properties of PDAAm Gels and the Substrates

substrate	substrate R_q (nm)	R_q of gel (nm)	gel E_{c1} (kPa)	gel E_{c2} (kPa)	gel friction coeff, μ^b
smooth silicon	0.9	5	89.5		0.1
		169[a]	28.4[a]	89.2[a]	0.007
rough silicon	103.9	72	96.0		0.1
polystyrene	2.60	140	2.8	3.7	0.004

[a] Gels containing linear polymer chains. [b] Measured at an angular velocity of 0.1 rad/s and a normal pressure of 1.7 kPa.

respectively, and their histograms are shown in Figure 1c and Figure 2c, respectively. The gel prepared on the silicon substrate shows a nice symmetric histogram of the elastic modulus, which is well described by a Gaussian distribution[14]

$$N = \frac{A}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(E - E_c)^2}{2\sigma^2}\right] \qquad (3)$$

Here, N is the number of events and E is the elastic modulus. E_c corresponds to the average of E, and σ is the standard deviation to E_c. The Gaussian distribution fitting of Figure 1c gives parameters of $E_c = 89.5$ kPa and $\sigma = 28$ kPa. The elastic modulus of the gel prepared on the PS substrate, however, shows two peaks in the histograms (Figure 2c), with peak values of 2.8 and 3.7 kPa, respectively.

To illustrate the correlation between height in the topographic image and modulus in the topographic image, randomly selected height and modulus profiles are shown in Figures 1d and 2d. The higher regions in the topographic image correspond to a softer elastic modulus in the elastic image, suggesting that the main peak at a lower value of E in Figure 2c corresponds to the higher regions in the topography image. These results show that the elastic modulus of the gel prepared on PS is about 30 times lower than gels prepared on silicon substrates. This is in agreement with the previous results obtained from microrheological investigations, showing that the PAAm gels prepared on the Teflon substrate have a lower local shear modulus and a higher local viscosity near the surface region.[8]

Accordingly, the gels prepared on the hydrophobic substrate have a rougher and softer surface in comparison with them prepared on hydrophilic substrates. The lower elastic modulus should be attributed to retardation of the polymerization reaction on the hydrophobic substrate which extensively suppresses the cross-linking reaction, resulting in a surface layer with many branched and dangling polymer chains, as reported in previous work.[6] The extensive increase in the surface roughness could be attributed to a larger free swelling of the surface layer of the gel that amplifies the substrate morphology, although the bulk gel hardly swells in water after gelation.

Surface Sliding Friction. In previous work, we have made systematic studies on the surface sliding friction of gels with various chemical structures.[12,13,15−18] It has been found that hydrogels exhibit a wide range of frictional coefficients μ, defined as the ratio of the frictional force to the normal load, on the order of 10^{-3} to 10° 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.[15] Relative sliding motions between two pieces of poly anionic gels, for example, exhibit frictional coefficients on the order of 10^{-2} in pure water due to the electrostatic repulsion between the gel surfaces.[12,13] It was further found that the sliding friction between

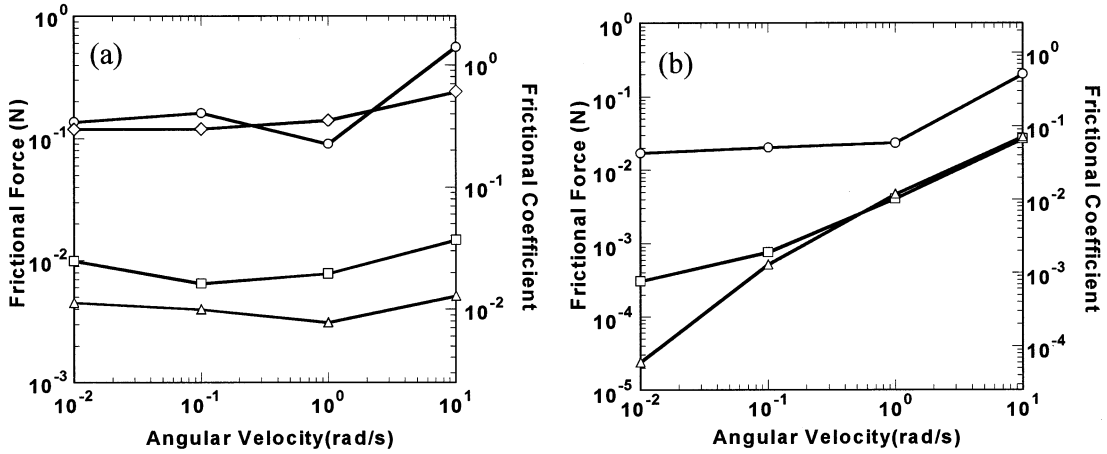

Figure 3. Angular velocity dependence of the frictional force and the frictional coefficient of gels in water. (a) PDMAAm gels at a normal pressure of 1.7 kPa: (○) synthesized on the smooth silicon, (◇) synthesized on the rough silicon, (△) synthesized on polystyrene substrate, and (□) containing linear polymer chains. (b) PAMPS gels at a normal pressure of 4 kPa: (○) synthesized on the smooth glass, (△) synthesized on polystyrene substrate, and (□) containing linear polymer chains.

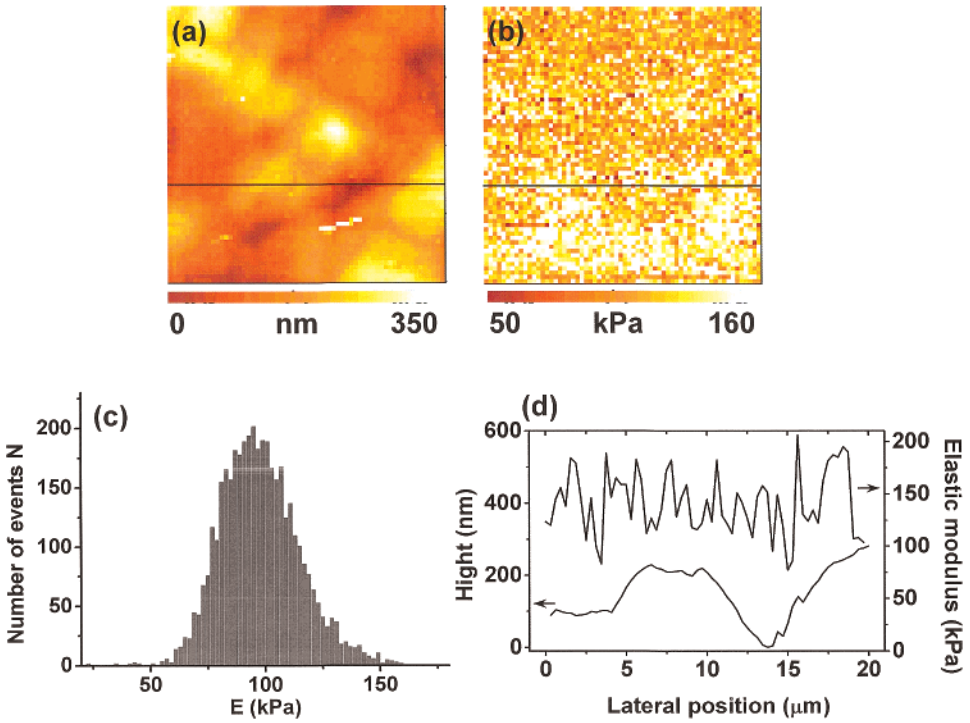

Figure 4. Topographical image (a), elastic modulus image (b), histogram of elastic modulus (c), and the height and modulus profiles (d) of a PDMAAm gel prepared on a rough silicon substrate. Data on the horizontal lines in parts a and b are plotted in part d. Scanning area: $20 \times 20\ \mu m^2$.

two same poly anion gels, PAMPS vs PAMPS, also sensitively changes with the substrate on which the gel is synthesized. PAMPS gels prepared on hydrophobic substrates showed a lower surface friction.

Figure 3a shows the velocity dependences of the surface sliding frictional force for PDMAAm gels prepared on a hydrophilic substrate of silicon and on a hydrophobic substrate of PS. For comparison, the results for PAMPS gels prepared on hydrophilic and hydrophobic substrates are also shown in Figure 3b. The PDMAAm gel prepared on PS has a lower surface friction than that of the gel prepared on hydrophilic substrate. This means that the substrate effect can be observed, not only for the friction between two polyelectrolyte gels carrying the same charges on the polymer network and producing an electrostatic repulsion at the interface, but also for neutral hydrogels.

Since the gels prepared on hydrophobic PS substrate show a much rougher and softer surface than gels prepared on hydrophilic silicon or glass substrates, the surface roughness and surface elastic modulus should be addressed individually when discussing the substrate effect on the surface friction of gels.

To investigate the effect of surface roughness on the friction, PDMAAm gels were synthesized on a rough silicon plate having a surface roughness of $R_q = 103.9$ nm. The morphological results of the gel are shown in Figure 4. By comparing Figure 4a with Figure 1a, it is clear that R_q of the gel surface synthesized on the flat silicon substrate is as low as 5 nm, while that synthesized on the rough silicon substrate is 72 nm, which is more than 10 times larger. Though the topographic images of the gel synthesized on the rough silicon substrate is quite different from that synthesized on the

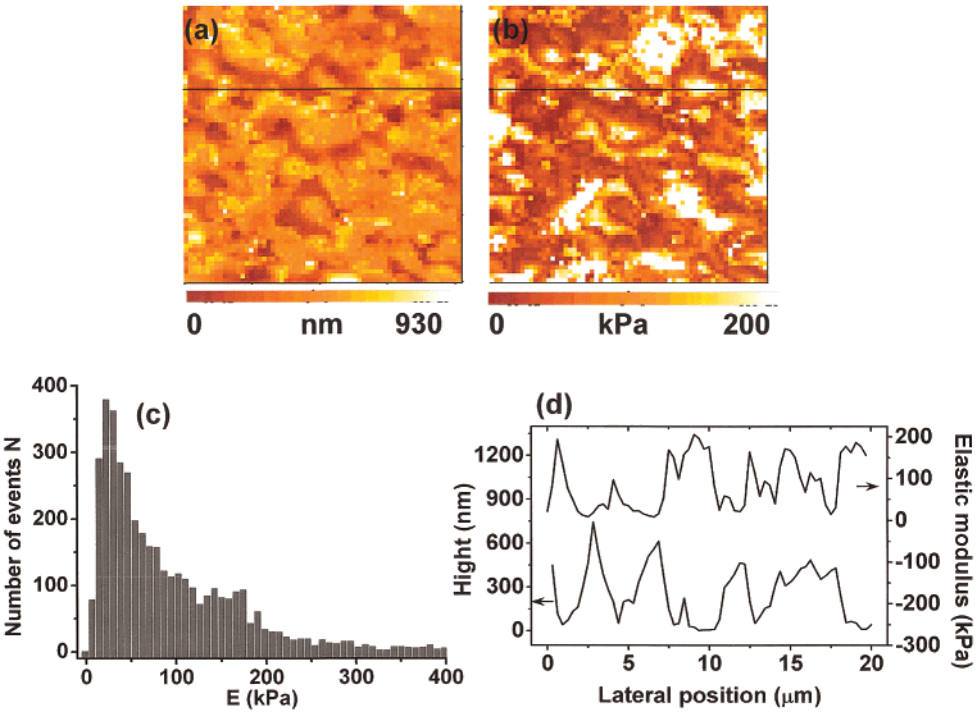

Figure 5. Topographical image (a), elastic modulus image (b), histogram of elastic modulus (c), and the height and modulus profiles (d) of a PDMAAm gel containing linear polymer chains. Data on the horizontal lines in parts a and b are plotted in part d. To clearly show the modulus image, the maximum scale marker range is set at a lower value than the maximum modulus value. Scanning area: $20 \times 20\ \mu m^2$.

smooth one, they show similar surface elastic modulus distributions, with almost the same average elastic modulus values (96 kPa for rough silicon and 89.5 kPa for smooth silicon). This can be clearly seen by comparing Figure 4, parts b and c, with Figure 1, parts b and c. No correlation is found between the topographical profile and the modulus profile, as expected (Figure 4d).

The above results indicate that the surface roughness of the hydrophilic substrate will be effectively replicated on the surface of gels, and the surface elastic modulus is independent of the surface roughness but dependent on the hydrophilic nature of the substrates.

The frictional behavior of the gel prepared on the rough silicon substrates is shown in Figure 3a. There is no distinct difference in the frictional behavior between gels with a rough surface and a smooth surface, if they are prepared on silicon substrates. Therefore, the difference observed for gels prepared on the PS substrate and silicon substrate is not attributed to their different surface roughness.

As has been elucidated in previous studies from the protein diffusion and microrheological studies,[3,8] the surface region of the gel prepared on the hydrophobic substrate consists of a loosely cross-linked network structure with many dangling chains. The decreased friction of the hydrogels prepared on the hydrophobic substrate has been attributed to the presence of brush-like dangling chains on the gel surface. To elucidate the effect of dangling chains on friction, gels containing free chains inside the network were also synthesized and their frictional behaviors studied. The free polymer chains existing near the gel surface may exert an effect similar to that of branched dangling chains in reducing the friction.

Figure 5 shows the surface topographical and elastic modulus results for the PDMAAm gel containing linear PDMAAm. The dangling chains are too soft to be sensed by the AFM tip which is much stiffer; that is why we can still observe the image of gels prepared on hydrophobic substrate with a high resolution. The surface elastic modulus of the gels increases when containing the linear polymer chains, due to entanglement of the linear chains with the polymer network, resulting in physical cross-linking and an increase in the modulus.

The AFM mapping of the elastic modulus yields average information to ca. 0.1−3 μm from the surface and cannot reveal the presence of the linear polymer chains that are assumed to exist on the surface of the gel in a thickness scale of the radius of one macromolecule. However, as shown in Figure 3, gels containing linear polymer chains show a almost the same frictional force as that for gels prepared on the PS substrate, regardless of the high elastic modulus, and this result was confirmed not only for the polyelectrolyte gels such as PAMPS, but also for the neutral gels of PDMAAm. The result demonstrates that one macromolecular layer of the dangling polymer chain is sufficient to dramatically reduce the surface friction of the gel.

The reduced frictional coefficients of the gel in the presence of the dangling polymer chains might be associated with the enhanced hydrodynamic thickness of the solvent layer. As discussed in previously,[16] when the interfacial interaction is repulsive between gel and substrate on which the gel is slid, a water layer is retained at the interface even under large normal loads resulting in a low friction. Though the neutral PDMAAm gels have no electrostatic repulsion at the sliding interface, the solvation of the polymer chains produces a hydrodynamic repulsion at the interface. 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 reducing the shear resistance.

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