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Microrheological Investigation of Substrate-Induced Gradient Structure in Hydrogels

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It has been recently reported[1−3] that the interfacial properties of hydrogels made by radical polymerization of water-soluble vinyl monomers depend on whether the substrate used for the preparation of the gel is hydrophobic (tetrafluoroethylene, polystyrene, hydrophobically modified glass, etc.) or hydrophilic (glass, mica, etc.). Gels synthesized on hydrophobic substrates exhibit a reduced friction coefficient against glass,[1] higher plant protoplast adhesion,[2] and enhanced diffusivity of proteins.[1] These results were interpreted by assuming that the surface of the gel made on a hydrophobic substrate consists of a loosely cross-linked network structure with dangling chains.

In situ monitoring of the refractive index change of solutions under polymerization reaction by electronic speckle pattern interferometry (ESPI) showed that during the gel formation a polymer concentration gradient is established over a spatial range extending up to 1 mm from the interface between the gel and the substrate.[4] However, the refractive index profile does not give information on the structural inhomogeneity of the gel, and the method is not applicable to gels with low concentration because of detection limitations.

Viscoelastic measurements in gels allow to probe directly the network structure since the presence of dangling chains should contribute to increase the local viscosity and decrease the modulus. In this note, we report on microrheological measurements by dynamic light scattering (DLS) of confined probe particles along the concentration gradient within the gel. First, we performed DLS measurements of bare gels. The experimental setup and the analysis of the data have been described elsewhere.[5] The total scattered intensity I_{tot} from a gel is the sum of two components: the fluctuating component I_F associated with the dynamic fluctuations of concentration, independent of the sample position in the gel, and the frozen-in component I_G corresponding to the static spatial fluctuations arising from nonrandom cross-linking. To measure these quantities as well as the correlation time τ of the dynamic concentration fluctuations, ensemble averages over many sample positions in the gel are performed. Figure 1 shows the variations of I_{tot}, I_F/I_{tot}, and τ along the height of polyacrylamide (PAAm) cylindrical gels for glass and tetrafluoroethylene (Teflon) substrates and for gels with different cross-linking densities. These quantities are found to be independent of the position in the gel for the glass substrate, whereas one observes a decrease of I_{tot} and an increase of I_F/I_{tot} and τ upon approaching the Teflon substrate. These observations confirm the results of ESPI measurements and suggest the formation of a gradient of cross-linking density over a range of several millimeters. The variations of I_{tot} can be almost entirely accounted for by those of the frozen in component. The latter increases with the cross-linking density, due to an enhancement of the structural inhomogeneities in the gel[6] (see Figure 1a,b). As for the correlation time, its increase in the vicinity of the substrate indicates an increased correlation length and therefore a larger swelling of the gel.

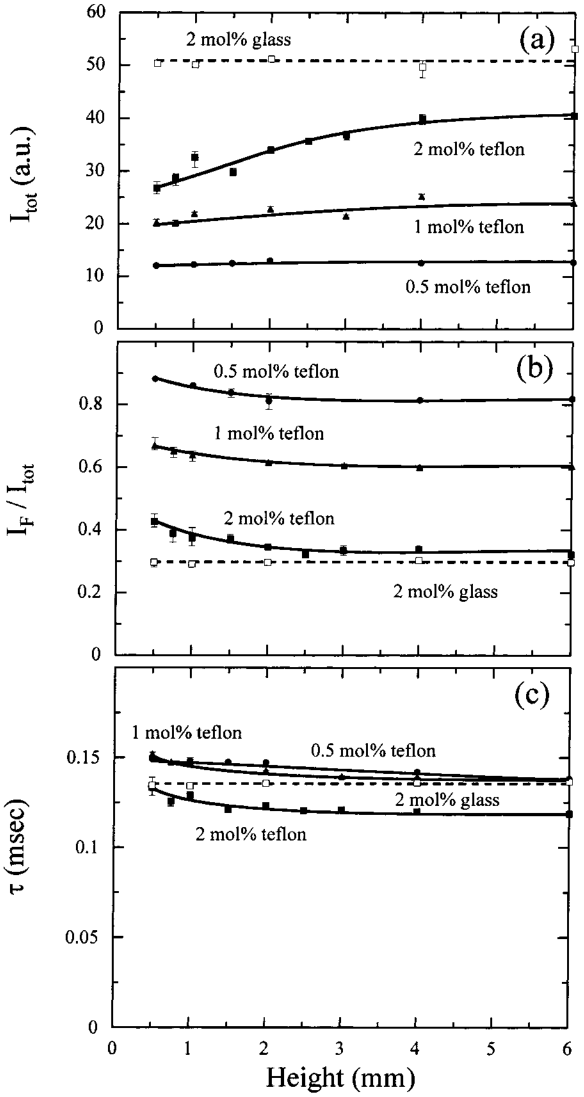

Figure 1. Height dependences of (a) total scattered intensity, (b) fraction of fluctuating part of the scattered intensity, and (c) correlation time for PAAm gels made on glass (open square) and Teflon (filled symbols). The amount of cross-linker and the nature of the substrate are indicated in the figure. The lines are guides for the eyes.

A more direct probe of the network structure is provided by measurements of the single scattering from a small amount of trapped particles dispersed within the gel before cross-linking reaction.[7] The mean-square displacement of trapped particles, with diameter much larger than the mesh size of the gel, is limited due to

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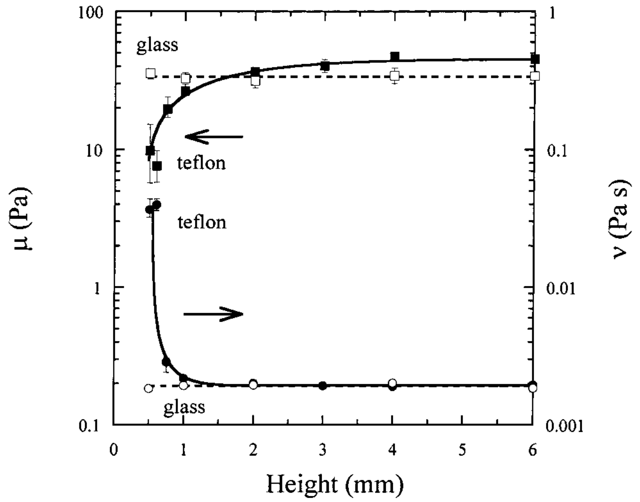

Figure 2. Height dependences of the local shear modulus μ and the local friction coefficient ν of PAAm gels (1 mol %) made on glass (open symbols) and Teflon (filled symbols).

the competition between the thermal energy of the particles and the elasticity of the network.[8,9]

The dynamic structure factor f does not go to zero at infinite time but levels off at an asymptotic value given by

$$\lim f(q,t) = \exp(-q^2\delta^2) \tag{1}$$

where q is the wave vector and δ is the size of the Brownian cage or characteristic spatial length explored by the particle. The local shear modulus μ of the gel probed by particles can be determined as follows with the assumption that the gel is an incompressible fluid,

$$\mu \cong \frac{k_B T}{6\pi R \delta^2} \tag{2}$$

where k_BT is thermal energy and R the radius of the particle. The above equation is obtained by arguing that the work necessary to move a bead of radius R by a distance Δr inside an elastic medium is of thermal origin.[9,10] From the decay rate of the correlation function one determines the characteristic time τ_c of the particle to explore the Brownian cage, which provides a measurement of the local friction coefficient ν that the particle experiences through the Stokes−Einstein equation:

$$\nu \cong \frac{k_B T \tau_c}{6\pi R \delta^2} \tag{3}$$

Height profiles of local shear modulus and local friction coefficient of the network are plotted in Figure 2. The shear modulus and the friction coefficient of the gel made on glass are independent of the distance to the substrate. On the other hand, the shear modulus of the gel made on Teflon decreases upon approaching the substrate. The shear modulus is reduced over a 4 mm depth, which is about the same range as the various quantities measured by DLS (Figure 1). This suggests that the cross-linking density of the network decreases in the vicinity of the interface since both the modulus and the scattered intensity depend on the cross-linking density. The friction coefficient of the network increases in a 1 mm thick layer close to the substrate. The local viscosity is likely to be less sensitive to the variation of cross-linking density except in the very close vicinity of the interface where the presence of many dangling chains might increase the friction exerted on the probe particles.

The results reported here confirm the intriguing observation that the hydrophobicity of the substrate perturbs the gelation process over a surprisingly large spatial range. They show unambiguously that the cross-linking density of the gel decreases upon getting away from the interface between the gel and the substrate. This is accompanied by an increase of the structural inhomogeneities in the gel. This study is also a striking illustration of the potential of the microrheological techniques to investigate the local viscoelasticity of materials.

References and Notes

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(5) PAAm gel was synthesized by redox radical polymerization of acrylamide (2.5%) in the presence of methylene bis(acrylamide) as a cross-linker (0.5−2 mol % of acrylamide), ammonium persulfate as an initiator (1 mM), and tetramethylethylenediamine as a redox initiator (0.6 vol %) under nitrogen atmosphere at room temperature. All the chemicals were used as received. Before the redox initiator was added, oxygen in the solution was removed by purging nitrogen for 5 min. All the solutions were filtered through 0.45 μm Millipore filter. For DLS measurements, the gel was prepared in a glass tube (12 mm in diameter). As a hydrophilic substrate, the bottom of the glass tube was used, and as a hydrophobic substrate, a piece of tetrafluoroethylene (Teflon) plate was set at the bottom. The glass tube and the Teflon plate were sonicated in ethanol and then in detergent aqueous solution followed by rinsing in distilled water. All the DLS measurements were made at 25 °C, at scattering angle 60°, triplicated and averaged. The scattering cell was vertically moved with a resolution of 10 μm from the surface of the substrate up to 6 mm within the gel. An arrangement using two pinholes (diameter 200 μm) and a lens in front of the photomultiplier provides a detection volume of (200 μm)^3. This determines the spatial resolution of the depth profiling.
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