

## Synchrotron infrared spectroscopy of water on polyelectrolyte brush surface

Polymers chemically grafted to the surface of substrates, known as polymer brushes, are often used to modify surface properties such as hydrophilicity or hydrophobicity, friction, and adhesiveness. Superhydrophilic surfaces are particularly attractive because of their potential applications to self-cleaning, antifogging, antifouling, and water lubrication systems. In this work, we examined the wettability of water on a cationic poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMTAC) brush prepared on a silicon wafer by contact angle measurement and synchrotron infrared (IR) spectroscopy [1].

The wettability of solids can be characterized by the spreading coefficient. The initial spreading coefficient,  $S_0$ , is defined as

$$S_0 = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} \quad (1)$$

Here,  $\gamma_{sv}$ ,  $\gamma_{lv}$ , and  $\gamma_{sl}$  are the interfacial tension at the solid/vapor, water/vapor, and solid/water interfaces, respectively. When  $S_0$  is positive, a water droplet deposited on a dry surface spreads and completely wets the surface. In contrast, a negative  $S_0$  value indicates partial wetting. A positive  $S_0$  value and, accordingly, the complete wetting state are expected for polyelectrolyte brush surfaces because they exhibit the extremely high  $\gamma_{sv}$  and quite low  $\gamma_{sl}$  values.

The contact angle measurement was carried out by reflection interference contrast microscopy. Monochromatic light ( $\lambda = 546$  nm) vertically irradiated onto a water droplet was reflected at the air/water surface or at the water/substrate interface. These two types of reflection create interference at the water surface, which enabled us to calculate the drop shape profile and determine the contact angle of water on the PMTAC brush (Fig. 1). The contact angle was extremely small but remained finite at  $0.95^\circ$ , contrary to our expectation based on the spreading coefficient.

The above results led us to a fundamental question: why is complete wetting not achieved, even with superhydrophilic polyelectrolyte brushes? To answer this question, we performed synchrotron IR spectroscopy at beamline BL43IR. A fine-focused IR beam from the synchrotron radiation was narrowed to  $10 \mu\text{m} \times 10 \mu\text{m}$  through an aperture. A small amount of water was deposited on the polyelectrolyte brush surface and dry air was gently passed around it to purge water vapor from the beam path. The IR spectra were obtained from the beam reflected from the inside and outside of a water droplet approximately  $10\text{--}50 \mu\text{m}$  away from the boundary (crosses in Fig. 1(a)). The representative spectra of water on the PMTAC brush are shown in Fig. 2. Inside the droplet, the spectrum had a broad peak centered at around  $3450 \text{ cm}^{-1}$ , which arose from the O–H stretching vibration (filled circles). This is a typical IR spectrum for water, and the broad shape reflects the diversity of the hydrogen bond network. Figure 2 also shows the spectrum obtained from the outside of the droplet (filled triangles). Intriguingly, even though the water phase was not visible under the microscope, weak O–H stretching absorption was detected. This was not from the vapor phase, which we confirmed was removed by purging with dry air in exactly the same setup. Furthermore, this small absorption was not seen at points sufficiently far from the droplet. Therefore, the absorption peak suggested the presence of a microscopic amount of water at the surface only in the vicinity of the droplet. Even more noteworthy is that, the position of the O–H stretching peak shifted from  $3450 \text{ cm}^{-1}$  to around  $3200 \text{ cm}^{-1}$ . This small peak was visible, even inside the droplet, as a slight shoulder on the main peak (arrow in Fig. 2). The peak shift to the lower wavenumber implied that the hydrogen bonds between the water molecules became shorter and that

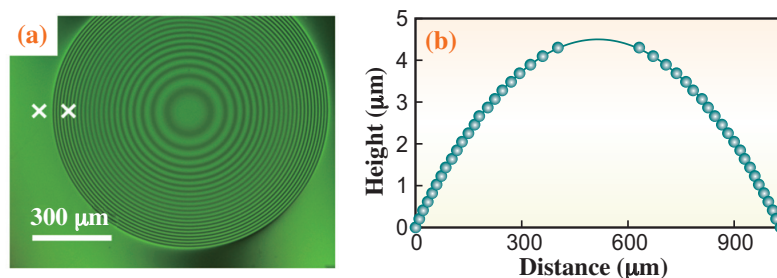


Fig. 1. (a) Interference rings of a water droplet on the surface of PMTAC brush. The crosses indicate the points measured by IR spectroscopy. (b) Drop profile calculated from the interference.

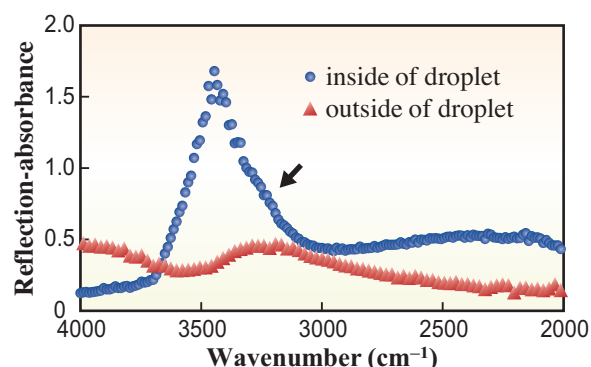


Fig. 2. IR spectra of water on the PMTAC brush: (●) inside and (▲) outside of the water droplet (see the crosses in Fig. 1). The outside spectrum is shown at 2× magnification for clarity.

the entire network became more rigid [2]. The peak at around 3200 cm<sup>-1</sup> has previously been observed for amorphous solid water [3]. We conclude that a thin layer of water, which included highly structured water, existed beneath and around the water droplet. The structuring of the water molecules can be attributed to both the spatial confinement in the thin layer and the hydration effect around the ionic species.

A schematic model of the wetting of the polyelectrolyte brushes is shown in Fig. 3. The initial spreading coefficient,  $S_0$ , is not valid for the wetting of a polyelectrolyte brush, because it assumes that the surface is dry and does not take the spreading and structuring of the water into consideration. Thus, we used the local equilibrium spreading coefficient,  $S$ , for the coexisting thin film.

$$S = \gamma_{sv}^{eq} - \gamma_{lv} - \gamma_{sl}^{eq} \quad (2)$$

The spontaneous penetration of water into the brush layer implied that the surface tension of the

wet brush,  $\gamma_{sv}^{eq}$ , is lower than that of the dry surface,  $\gamma_{sv}$ . This is mainly due to the enthalpy and entropy of the mixing of the polymer and water, and the surface rearrangement of  $\alpha$ -methyl groups, which have relatively low surface energy, caused by the high flexibility of polymer chains in the wet brush. Furthermore, the solid/water interfacial tension after the structuring of water,  $\gamma_{sl}^{eq}$ , should be much higher than  $\gamma_{s1}$ , which is expected to be extremely low because the thermodynamic properties of structural water resemble those of ice rather than liquid water. It has been reported that the interfacial tension at the ice/water interface is fairly [4]. These two effects result in  $S < S_0$  and an increase in the contact angle, which breaks the conditions for complete wetting. Therefore, we concluded that a thin layer composed of the swollen polymers and the structural water existed under and even outside the droplet, and prevented the complete wetting of the highly hydrophilic polyelectrolyte brushes.

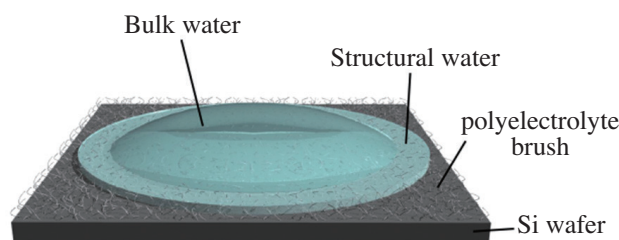


Fig. 3. Schematic illustration of the wetting of a polyelectrolyte brush.

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#### References

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