Optical mapping of the evolution of water content during the swelling of hydrophilic polymers

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S1. Preparation of the PAA/PEO hydrogel

The hydrogel was made by firstly mixing the aqueous solution (100mL, 4mg/mL, pH 2.5) of Poly (acrylic acid) (PAA, Mw 450k) and poly (ethylene oxide) (PEO, Mw 600k) through peristaltic pumps at a flow rate of 5 mL/min under stirring. The precipitation was then collected and pressed into film. Finally, the hydrogel was obtained after further dried in the oven for 24 hours. Poly (acrylic acid) and poly (ethylene oxide) were purchased from Sigma-Aldrich.

S2. Detailed description for calculating the critical angle of hydrogel

First, the optical intensity of each pixel in the image or the whole image versus the incident angle is automatically extracted by MATLAB (Figure S1a). The angle with the maximum optical intensity change is defined as the critical angle herein. Hence, the curve of differential optical intensity versus time is then obtained and shown in Figure S1b (black lines). To obtain a more accurate value of the critical angle, the curve is further fitted by a Gaussian function (red lines), where the red arrows indicated the final calculated critical angle of this condition.

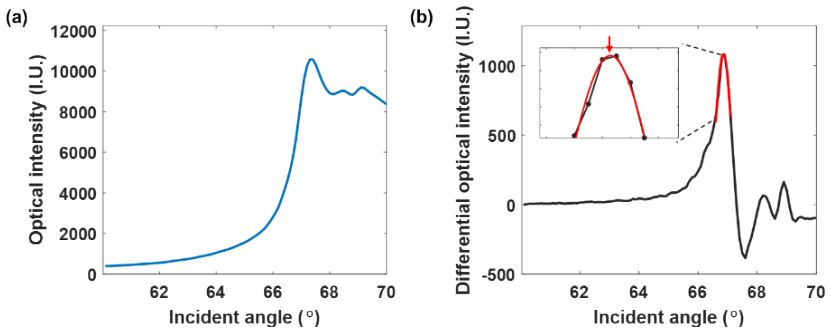

Figure S1. (a) Angle-dependent optical TIRM intensity of one pixel in an image shown in Figure 1b. (b) Plot of the corresponding differential optical intensity versus incident angle (black). The red line shows the gaussian fitting result and the red arrow indicates the final obtained critical angle.

S3. Sensitivity assessment of refractive index measurement with the total internal reflection microscopy (TIRM)

Four different concentrations of ethanol-water mixtures were measured sequentially by built TIRM, with which water weight percents are 89.48, 90.67, 91.94, and 93.31, respectively. Although the RI of the four mixtures only change from 1.3393 to 1.3368,[1] the gradually increased critical angles for TIR were clearly observed in their incident angle-dependent optical intensity curves (Figure S2a). Then, the standard deviation of the obtained critical angle was further determined to be 0.003° by measuring the same ethanol-water mixtures three times (Figure S2b-c). Therefore, a change in critical angle of ~0.01° (3*STD) and a corresponding change in RI of ~0.0002 is detectable herein. It's worth noting that the critical angle herein was extracted by fitting the curve of differential optical intensity versus incident angle (Figure S1), which contributes to improving the sensitivity of critical angle extraction and exceeding the instrument limit of 0.1° minimum angle scanning step.

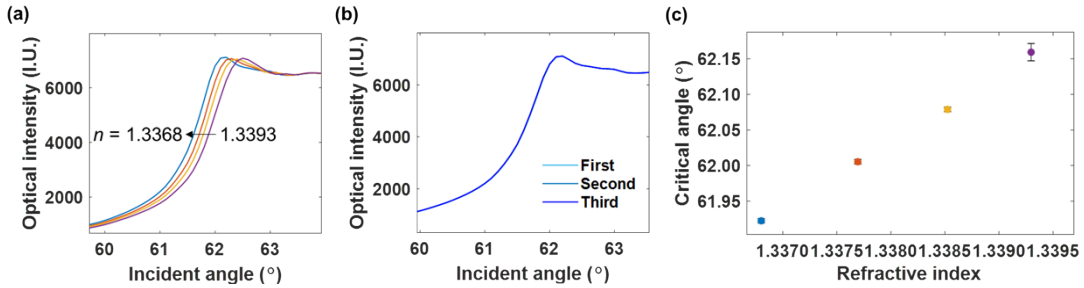

Figure S2. (a) Angle-dependent optical TIRM intensity curves of ethanol-water mixtures with different water weight percents (blue line: 93.31, orange line: 91.94, yellow line: 90.67, purple line: 89.48). (b) The three consecutive measurements of angle-dependent optical TIRM intensity curves of ethanol-water mixtures with water weight percents of 93.31. (c) Errorbar plot of the critical angle versus their refractive index of the four ethanol-water mixtures.

S4. Selected TIRM images of the hydrogel during swelling process

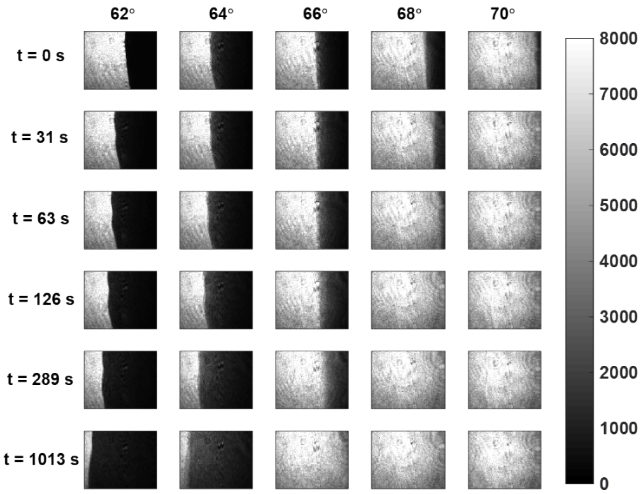

Figure S3. Selected TIRM images of the hydrogel acquired under different incident angles at several moments during the swelling process. The hydrogels brighten from left to right during the angular scan (the water was supplied on the left edge of the hydrogel), indicating the higher water content of the left region of the hydrogel at a moment.

S5. Water content distribution in the drying process of hydrogel film

To investigate the drying process, the water source at the left edge was removed after the hydrophilic polymer has absorbed enough water for 20 minutes. When the left edge of the hydrogel came into contact with the dry air, its water content immediately decreased (Figure S4). An increased concentration distribution gradient of water content within hydrogel from its left edge to right gradually formed, which is opposite to the distribution formed in the wetting process.

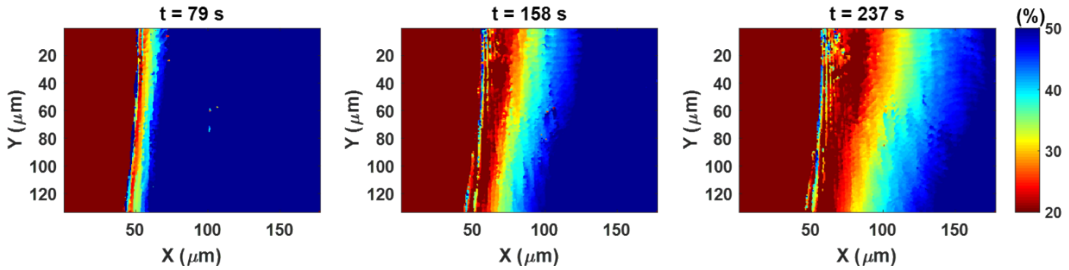

Figure S4. Water content distribution within hydrogel during the drying process.

Reference

1. T. A. Scott, Jr., *The Journal of Physical Chemistry*, 1946, **50**, 406-412.

Movie S1. The TIRM images of the hydrogel before and after swelling during the incident angle scanning.