Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Directional control of diffusion and swelling in megamolecular polysaccharide hydrogels

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Supporting Movie S1: Side view of the swelling process under cross-polarized light. 300 times actual speed. The width of the gel sample is ~4 mm.

EXPERIMENTAL SECTION

Materials. *Sacran* was extracted from *Aphanothece sacrum* as per the procedure described in a previous study.

Preparation of gels. 0.5% *sacran* solution was prepared by dissolving *sacran* fibers obtained from *Aphanothece sacrum* in pure water (< 80˚C) on a magnetic stirrer for ~12 hours. The resulting solution (~50 mL) was then poured into a 5 cm × 5 cm polypropylene case and kept in a temperature regulated oven at 60 ˚C for 24 hours with continuous air purging to prepare a dried thin film. The films were then annealed at 80 °C, 100 ˚C and 120 ˚C for 2 hours to obtain the required crosslinked gel films, which were left at ~25 ˚C to be used for swelling and kinetics experiments.

SEM observation. The dried polymer films were observed by scanning electron microscopy (Hitachi, S-4500) without any metal modification.

Measurements of swelling kinetics. The swelling kinetics of the hydrogel was measured from a dried state to a wet state in a pH 7 buffer solution for a duration of 24 hours, and their swelling rate was evaluated. The parameters, relaxation time (τ) and diffusion coefficient (D) were then calculated using the following equations.[1-3]

$$\ln\left[\frac{L_\infty - L(t)}{L_\infty - L_0}\right] \approx -\frac{1}{\tau}t + \ln\left[\frac{6}{\pi^2}\right] \quad (1)$$

$$D = \frac{L_{z\infty}^2}{\pi^2 \tau} \quad (2)$$

Measurements of swelling ratio. Samples were cut and kept in pH 8 buffer solution for 16 hours after measuring their initial thickness at ~25 ˚C. The change in length and thickness of the sample was analyzed using a cross-nicol polarimeter. Next, the sample was transferred to buffer solutions of decreasing pH for over 45 minutes. The same procedure was repeated until swelling measurements were made in pH 2.2 buffer solution. The buffer solutions (pH 2.2—8.0) were controlled by mixtures of citric acid and Na_2HPO_4. The swelling ratio was calculated by normalizing the dimensions at a given pH with the initial dimensions, L_0. This swelling ratio was eventually plotted against pH to obtain the equilibrium swelling graph.

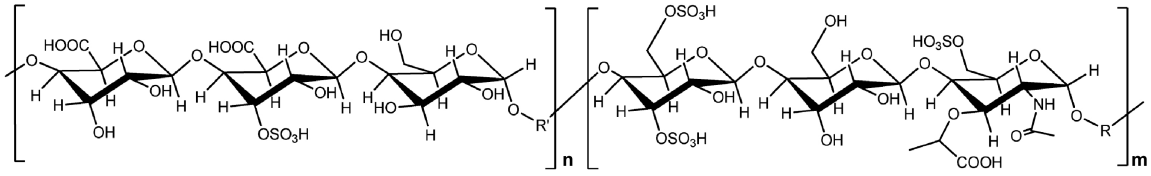

Figure S1. Chemical structure of *sacran*.

Elemental analyses and chromatographic and spectroscopic studies of *sacran* revealed the following sugar residues: Glc, Gal, Man, Fuc, Rha, Xyl, Rib, methylated hexose, uronic acids, and trace muramic acid. The carboxylate composition of *sacran* was 11 mol%, and substitution of sulphate groups was favoured when the sulphate composition was 22 mol% with sugar residues.

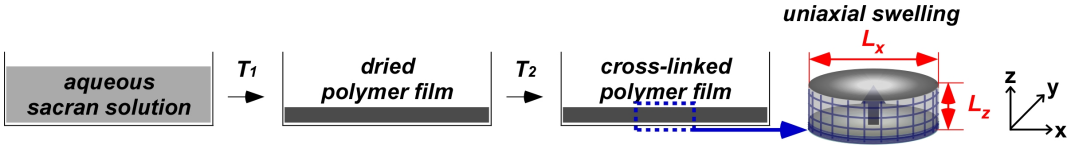

Figure S2. Schematic illustration of preparation of polymer film and introduction of crosslinks.

An aqueous *sacran* solution is dried at T_1 as the first step, and the dried polymer film is annealed to introduce crosslinking points as the second step ($T_2 > T_1$).

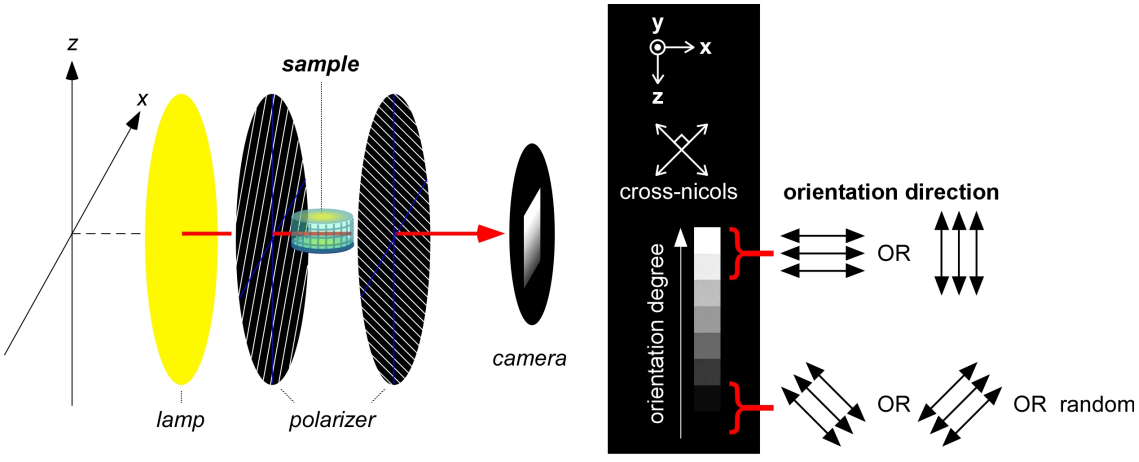

Figure S3. Schematic illustration of the experimental setup used for observations under cross-polarized light. The polarizers were normally adjusted to 45° and 135°. The transmitted light intensity was analysed by ImageJ to evaluate the degree of orientation.

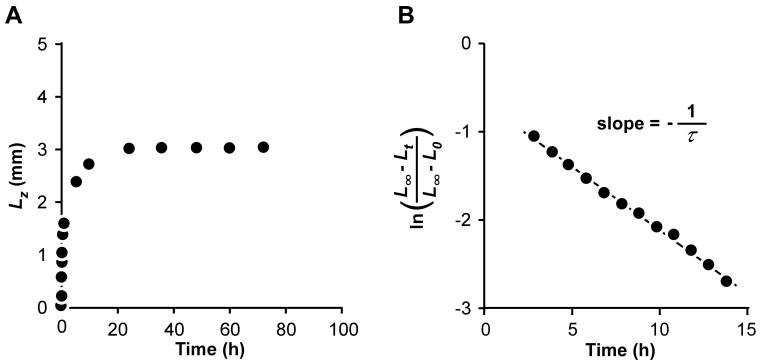

***Figure S4*. A.** Swelling kinetics in the Z-direction of *sacran* gels from dried state to wet state at pH7 over 3 days. **B.** The linear plot obtained after solving equation (1).

$$\ln\left[\frac{L_\infty - L(t)}{L_\infty - L_0}\right] \approx -\frac{1}{\tau}t + \ln\left[\frac{6}{\pi^2}\right] \qquad (1)$$

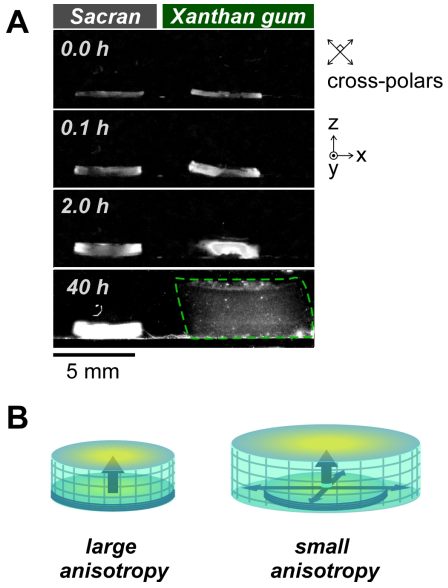

***Figure S5*.** Swelling process of *sacran* hydrogel and *xanthan gum* hydrogel observed under cross-polarized light. The polymer films were annealed at 80 ˚C.

The ratio along the x-axis and y-axis was approximately same value. Precisely, the hydrogels sometimes show a small warp in three-dimensional (Fig. S5). By checking the width from three side directions, the dispersions were confirmed to be less than 10%.

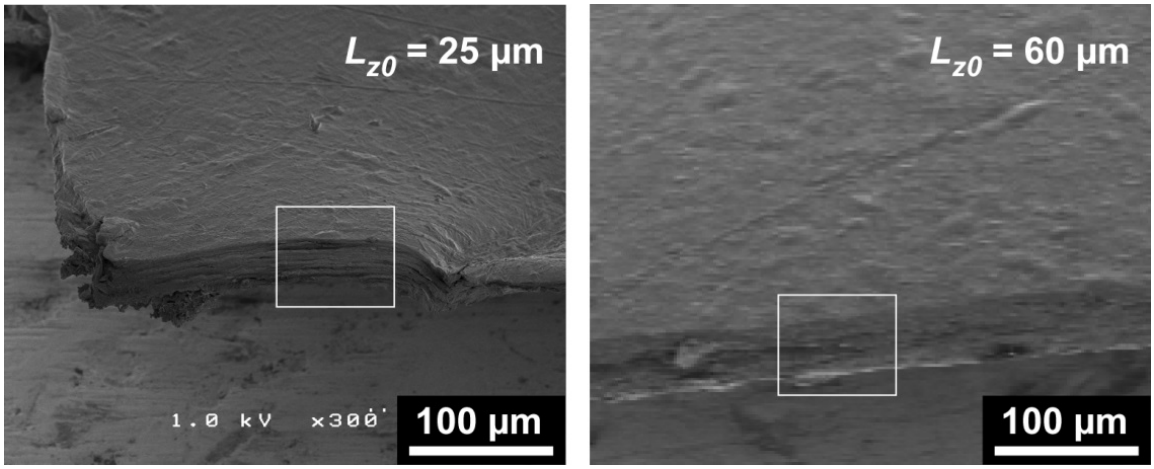

Figure S6. SEM images of *sacran* dried films at given initial thickness.

References

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2 H. Tanaka, *Phys. Rev. Lett.* 1992, **68**, 2794.
3 J. Yoon, S. Cai, Z. Suo, R. C. Hayward, *Soft Matter*, 2010, **6**, 6004.