Supplementary Information

Anisotropic Swelling in Hydrogels Formed by Cooperatively Aligned Megamolecules

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Fig. S1 Main structure of sacran chains where the sequences in monosaccharide triads, fashion of glycoside linkages, steric conformations of hydroxyls or other substitutes are tentative.



Fig. S2 Intensity change of light transmitting through a sacran solution under cross-nicol polarimetry. The measurement was made under rotational shear at an angular velocity of 10⁴ rpm in order to generate liquid crystalline mono-domains. Inset picture is a polarized microscopic image of sacran aqueous solution with a concentration of 0.5 wt% in liquid crystalline state.



Fig.S3 Absolute weight-average molecular weight, M_w , of sacran chains, determined by multi-angle static laser light scattering (MALLS), where sacran chains were divided by size exclusion chromatography (chromatograms are recorded by a RI detecter). Time shown top of each figure are ultrasonic irradiation time to sacran solution with a concentration of 0.5 wt%.



Fig. S4 MALLS plots of sacran solution in NaNO₃ aq (0.1 M). Plots were fit by Zimm models. Coefficients of determination, R^2 , are shown at the bottom of each plot. Time shown top of each figure are ultrasonic irradiation time to sacran solution with a concentration of 0.5 wt%. θ and C are scattering angle and concentration f sacran solution, respectively, and R (θ) is the excess Rayleigh ratio of the solution as a function of θ . K is the constant of $\pi^2(dn/dc)^2 n_0^2/N_a \lambda_0^4$, where N_a is Avogadro's number, n_0 is the refraction index of water (1.331), λ_0 is the vacuum wavelength of the laser (658 nm), and dn/dc of sacran is estimated as 0.108 mL/g.



Fig. S5. Degital images of water-swollen hydrogels prepared from the films annealed at 140 $^{\circ}$ C. The images were taked before (left) and after (right) the hydrogels were annealed in water at 80 $^{\circ}$ C for 48 hours.



Fig. S6. Cross-sectional views of sacran solution in drying process under cross-polarized light. The sample was placed in a quartz cuvette ($10 \times 5 \times 5 \text{ mm}$). Initial concentration of sacran: 0.5 wt%. Drying temperature was 60 °C.



Fig. S7. The mechanical data were obtained by two modes. One is a compression mode illustrated in **a** for the hydrogels from the film annealed at 70, 80, 90, 100 $^{\circ}$ C, the other is an elongation mode shown in **b** for the hydrogels from the films annealed at 100, 120, 140 $^{\circ}$ C. The data were summarized in Table 1.

Temp. (°C)	$q_{_{ m xy}}$	$q_{_{ m z}}$	$q_{ m z}^{~}/q_{ m xy}^{~}$
70	1.73	120	69
80	1.48	75	51
90	1.23	46	38
100	1.18	39	33
120	1.03	17	17
140	1.02	14	13

Table S1. Anisotropy of linear swelling degree of thickness to width in sacran hydrogels

Table S2. Anisotropy of linear swelling degree of thickness to width and swelling degrees of sacran hydrogels with various thicknesses of precursor film

thickness (µm)	$q_{_{ m xy}}$	$q_{_{ m Z}}$	$q_{_{ m z}}^{~}/q_{_{ m xy}}^{~}$	q
70	1.23	28.8	24	38
60	1.18	30.7	25	39
50	1.22	35.9	28	42