Supplementary information

for

A Diffusion-Driven Fabrication Technique for Anisotropic Tubular Hydrogels

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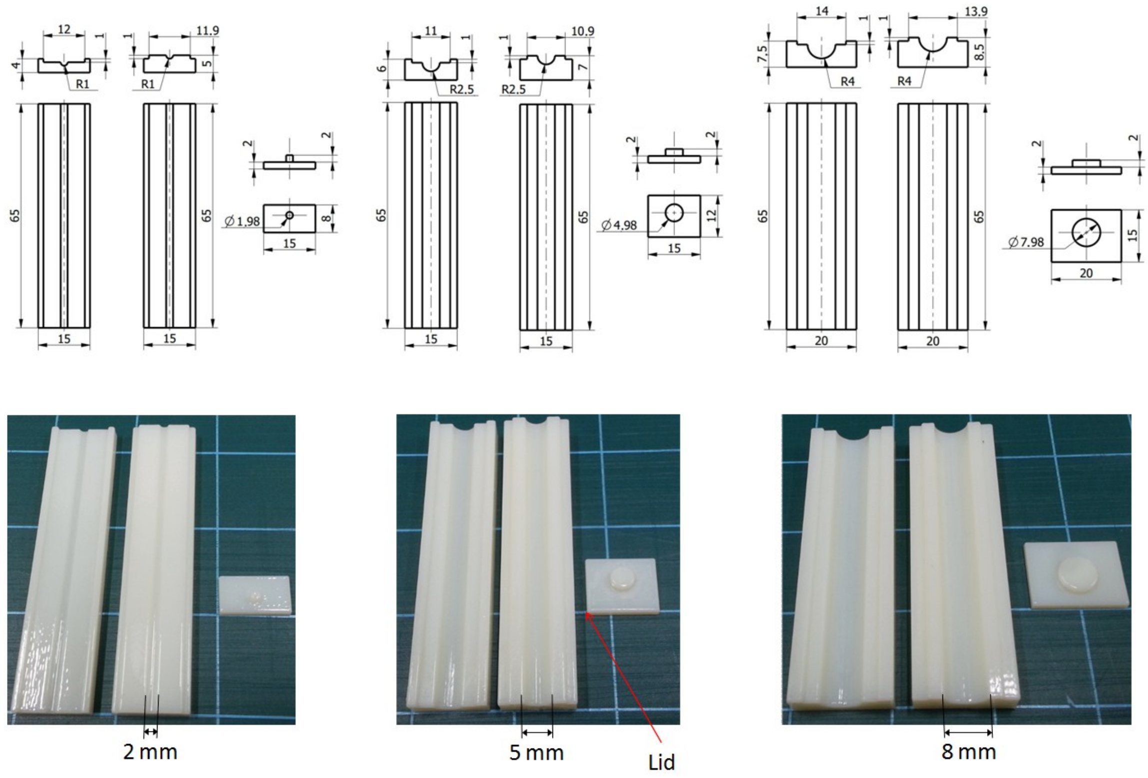


Figure S1. 3D printed molds used for the preparation of the cylindrical core polyacrylamide (PAAm) hydrogels. The internal core diameters were 2 mm, 5 mm, and 8 mm. Both a schematic and a photograph of each mold are shown.

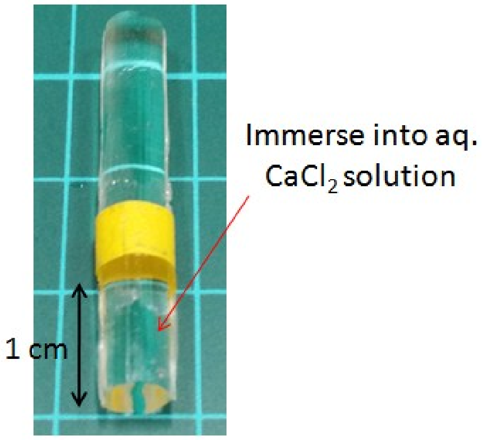


Figure S2. Preparation of a core gel (diameter: 5 mm) with a pre-programmed ion concentration gradient. A 1 cm length of the core gel was immersed in 1 M *aq*. $CaCl_2$ for 5 min and used to fabricate a tubular gel with a low wall thickness gradient as shown in Figure 2b(i). Yellow vinyl tape was attached to the core gel surface to protect the boundary region of the core gel during immersion in the ion solution. For the high wall thickness gradient, a 1 cm length of the core gel was immersed in 2 M *aq*. $CaCl_2$ for 5 min and used to fabricate a tubular gel as shown in Figure 2b(ii). To prepare a core gel with a high and low concentration gradient, a 1 cm length of the core gel was immersed in 2 M *aq*. $CaCl_2$ for 5 min and then, after moving the vinyl tape 1 cm higher on the core surface, the full 2 cm length was immersed in 2 M *aq*. $CaCl_2$ for 30 s. This core gel was used to fabricate the tubular gel shown in Figure 2b(iii).

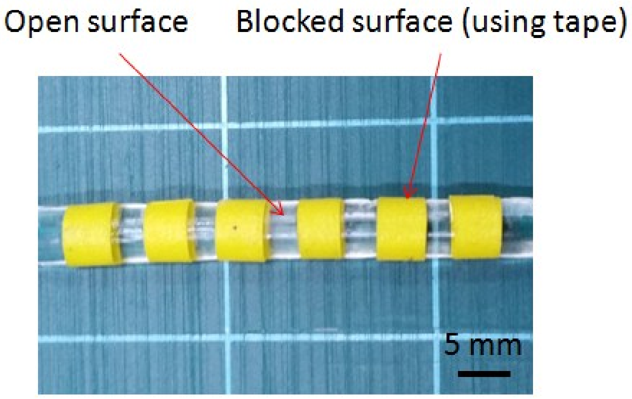


Figure S3. Preparation of a core gel with an ion concentration gradient for fabrication of a hydrogel tube with a wavy surface. Vinyl tape was used to prevent contact with the ion solution. The patterned core gel (diameter: 5 mm) was immersed in 1 M *aq*. $CaCl_2$ for 5 min. Firstly, the ions penetrated through the open surface. Then, the ions in the open regions of the gel traveled toward the blocked regions of the gel to create an ion concentration gradient with a maximum concentration at the centers of the open regions and a minimum concentration at the centers of the blocked regions. The distance between two points of maximum or minimum concentration was 8 mm. Then, the tape of the core gel was removed and the core gel was used for the preparation of a tubular gel with a wave-like surface pattern.

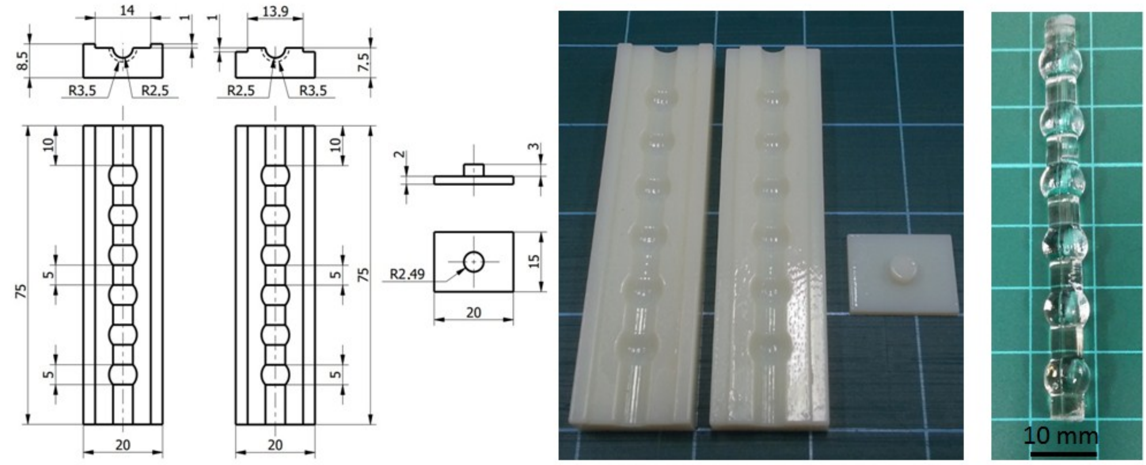


Figure S4. Schematic (left) and photograph (middle) of the 3D printed mold used for the preparation of a PAAm core hydrogel (right) with a periodic variation in diameter.

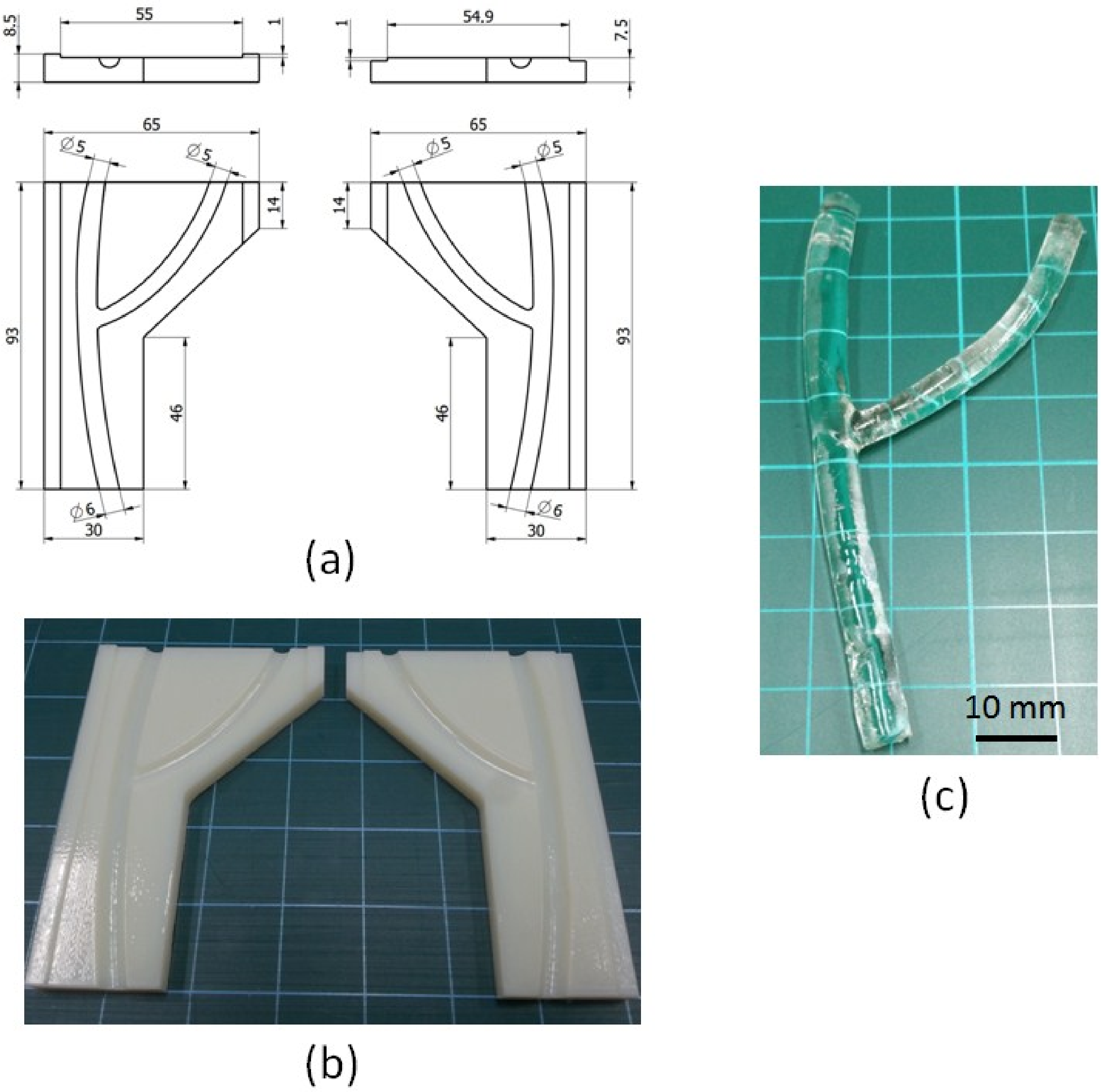


Figure S5. Schematic (a) and photograph (b) of the 3D printed mold used for the preparation of a PAAm core gel with a branched architecture (c). This core gel was used to fabricate a branched tubular hydrogel.

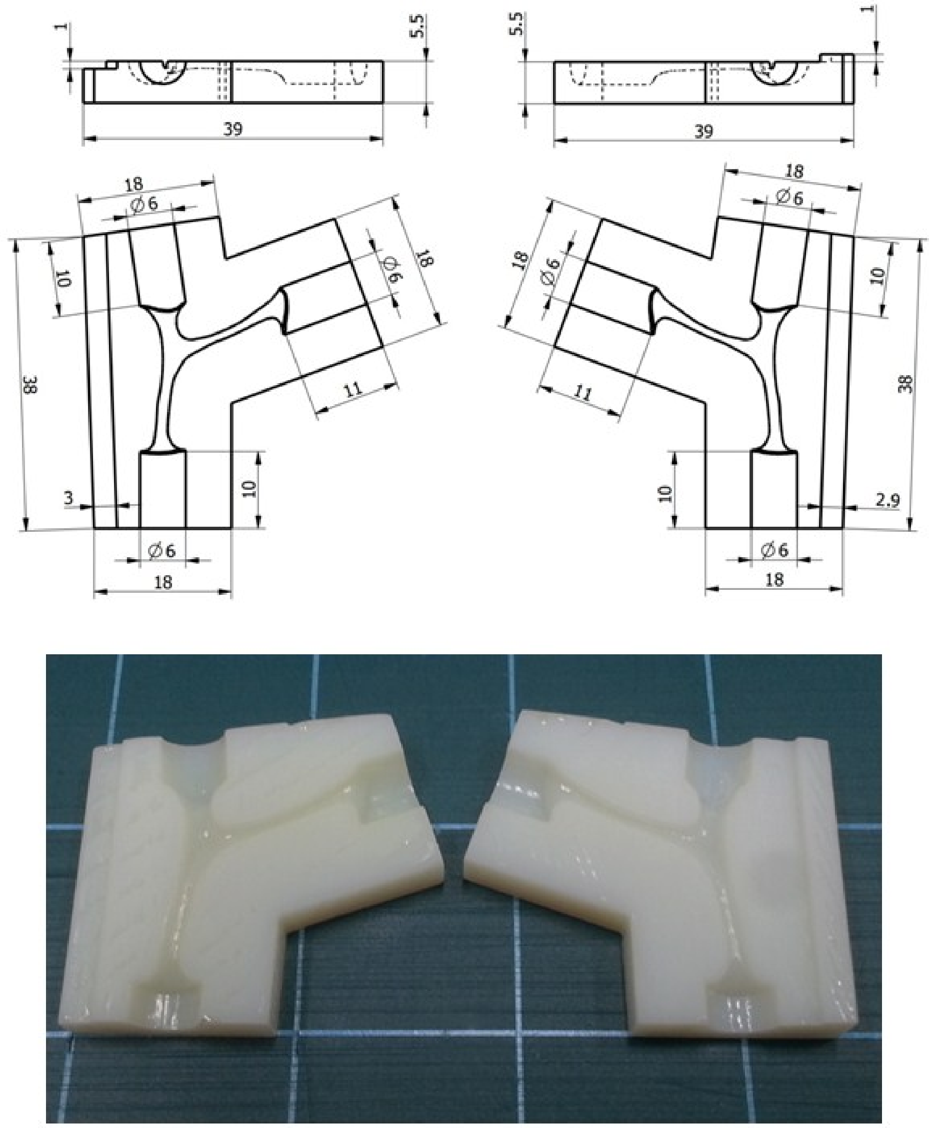


Figure S6. Schematic (upper) and photograph (lower) of the 3D printed mold used to fabricate a PAAm core gel for a prostate-shaped hydrogel.

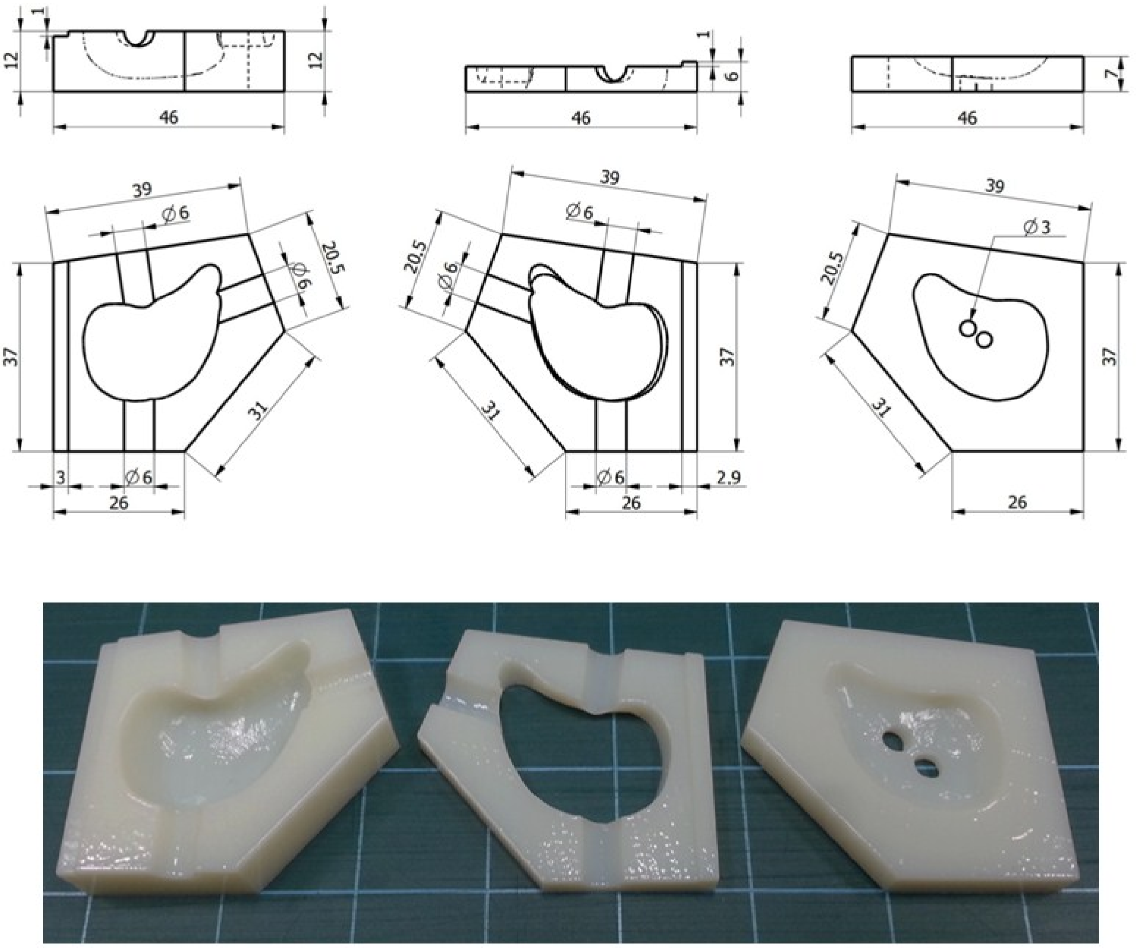


Figure S7. Schematic (upper) and photograph (lower) of the 3D printed mold used to fabricate a prostate-shaped hydrogel.

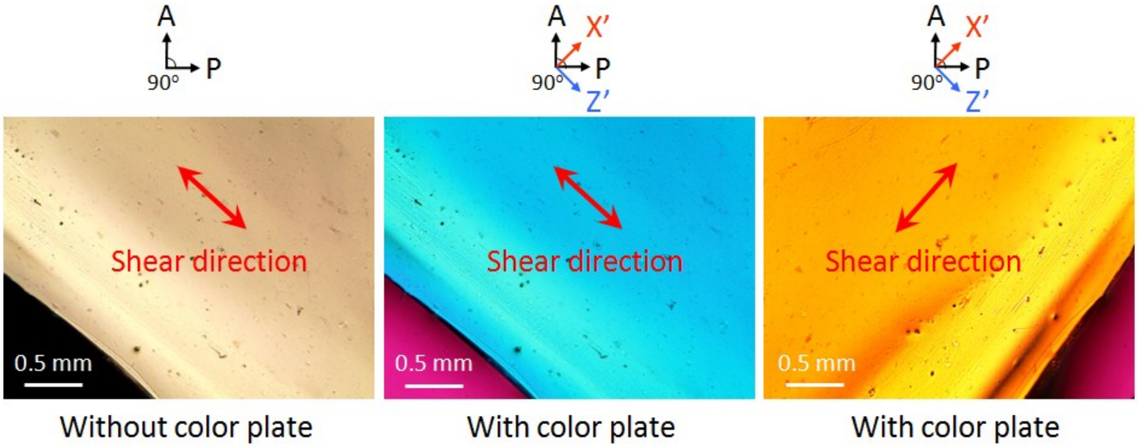
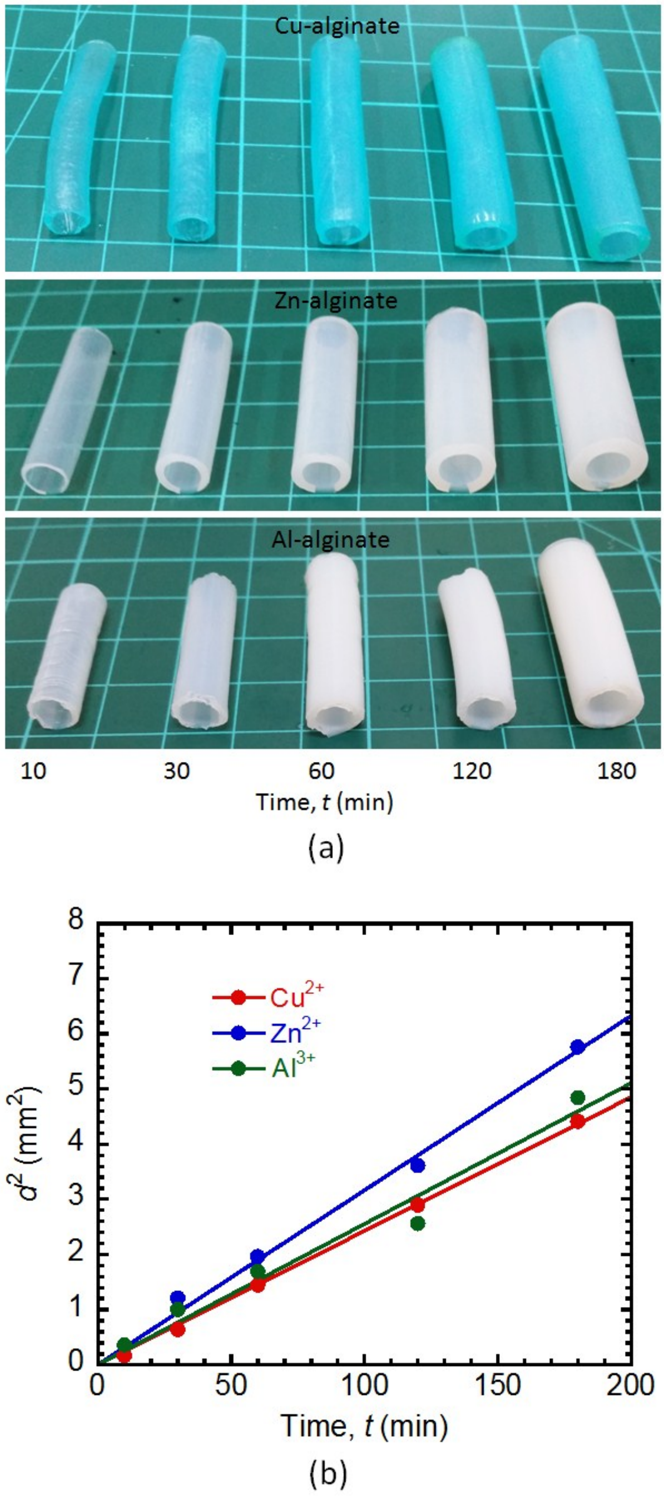


Figure S8. Determination of the optical property of alginate. Polarizing optical microscopic (POM) images of a sample prepared by translational shearing (by dragging with glass plate) of a 5 wt% Na-alginate solution and subsequent fixation of the structure in the presence of 0.5 M $CaCl_2$ for 1 min. The photographs were taken using crossed polarizers, with and without a 530-nm color plate. A: analyzer, P: polarizer, X' and Z': fast and slow axes of the color plate, respectively. First-order birefringence (grey white) of alginate was increased (additive birefringence: blue color) by the insertion of a 530-nm color plate along the shear direction, and decreased (subtractive birefringence: orange color) when the color plate was placed perpendicular to the shear direction. These results indicate that alginate polymer has positive birefringence.



(a)

(b)

Figure S9. (a) Photographs of the Cu-alginate, Zn-alginate and Al-alginate hydrogel tubes (core diameter: ~5.5 mm) prepared by the radial diffusion of 0.5 M ion from a PAAm core gel (diameter: 5 mm) through a 3 wt% Na-alginate aqueous solution. (b) The linear relationship between the square of the wall thickness (d^2) and gelation time (t).

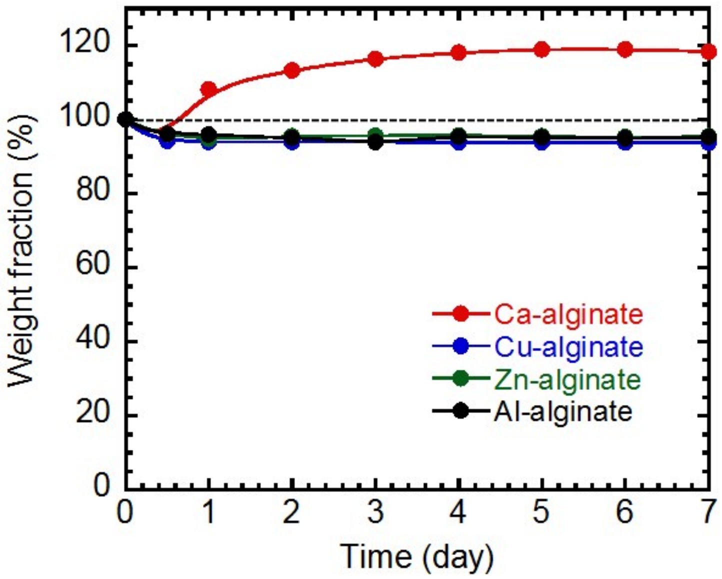


Figure S10. The stability of Ca-alginate, Cu-alginate, Zn-alginate and Al-alginate tubular gels in water. All the gels were prepared by the diffusion of 0.5 M metal ion from the core hydrogel (diameter: 5 mm) through a 3 wt% alginate solution for 2 h.

Table S1. Water contents of the Ca-alginate hydrogels prepared herein.

Ca-alginate hydrogels		Water contents in the final hydrogels (wt%)
[Alginate] (wt%)	[Ca^{2+}] (M)	
3	0.5	95.1 ± 0.4
4	0.5	93.3 ± 0.3
5	0.5	91.4 ± 0.2
5	0.1	91.2 ± 0.1
5	1	92.4 ± 0.1

Table S2. Comparison of mechanical properties of Ca-alginate hydrogels prepared in this study with the reported Ca-alginate gels in previous studies.[S1-S4]

[Alginate] (wt%)	[Ca^{2+}] (M)	Young's modulus (MPa)	Tensile strength (MPa)	Remarks
2.4 – 2.7	0.02 – 0.05	0.02 – 0.17	0.01 – 0.05	Reference S1
4	0.5	0.39 ± 0.05	0.32 ± 0.03	Reference S2
2.5 – 5	1 – 5	0.15 – 0.55	–	Reference S3
2	1.5	0.003 – 0.115	0.002 – 0.085	Reference S4
3 – 5	0.1 – 1	0.87 – 2.54	0.31 – 1.16	This study

Table S3. Comparison of mechanical properties of tubular hydrogels prepared in this study with various reported gels in previous studies.[S5-S7]

Hydrogels	Fabrication method	Young's modulus (MPa)	Tensile strength (MPa)	Remarks
Cellulose nanofibrils	Solution extrusion	0.055 – 0.504	0.005 – 0.054	Reference S5
Ca-alginate	3D printing	0.1	0.025	Reference S6
Fibrin	Molding	0.01 – 0.03	0.01 – 0.04	Reference S7
Collagen	Molding	0.012	0.005	Reference S7
Ca-alginate	Diffusion	0.87 – 2.54	0.31 – 1.16	This study
Cu-alginate	Diffusion	13.7 ± 0.3	3.2 ± 0.3	This study
Zn-alginate	Diffusion	10 ± 4.3	3.6 ± 0.7	This study
Al-alginate	Diffusion	40 ± 3.4	2.7 ± 0.4	This study

References

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