Supporting Information

Preparation of 4D Hydrogel with PET-RAFT and Orthogonal Photo-reaction

Chanhyuk Jee[a], Hikaru Matsumoto[a], Tasuku Horiuchi[a], Zaiyang Liu[b], Zhongkui Wang[b], Obayashi Kakeru[c] Ken Kojio[d], Masanori Nagao[a] and Yoshiko Miura[a]*

a.Department of Chemical Engineering, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, Japan, 819-0395.

b.Department of Robotics, Ritsumeikan University, Kusatsu 525–8577, Japan

c.Institute for Materials Chemistry and Engineering,KyushuUniversity,Fukuoka819-0395,Japan

*Corresponding authors:

Prof. Yoshiko Miura

E-mail: miuray@chem-eng.kyushu-u.ac.jp

Tel: +81-92-802-2749

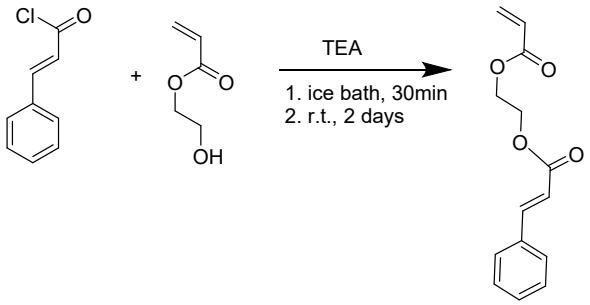
Fax: +81-92-802-2769

1. **Monomer synthesis**
2. **Physical properties of hydrogels**
3. **Experimental conditions**

1. Synthesis

a) Synthesis of cinnamoyl ethyl acrylate (CEA)

Scheme S1. Synthesis of cinnamoyl ethyl acrylate (CEA).



5.6 g (48 mmol) of 2-hydroxyethylacrylate (2-HEA), 3.3 g (32 mmol) Triethylamine (TEA) were dissolved in 40 ml of solvent, THF, and made N_2 atmosphere by nitrogen purging in 3-neck flask with stirring by magnetic bar in ice bath for made 0 C condition. At the same time, 7 g(42 mmol) of Cinnamoyl chloride dissolved in 20 ml of THF completely then dropped slowly by dropping funnel for 10min to prepared 3-neck glass setting. After dropping time was overreacted 3 hours in ice bath then 21 hour in room temperature. The reaction mixture was evaporated, and dissolved in CH_2Cl_2 100 mL. The solution was washed with MillQ water for 3 times. TEA-HCl salt was filtered and the reaction mixture was purified by silica gel chromatography (Biotage: EtOAc:hexane (gradient)) and the solution was removed by evaporator to get the yellow liquid . The product was analyzed by ^{1}H-NMR.

Yield 3.58 g , 28.4 %

a-1) NMR peak of CEA's

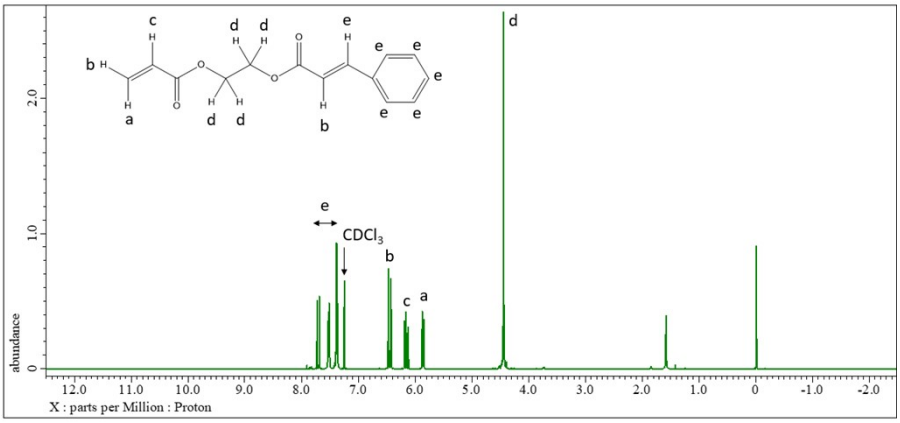
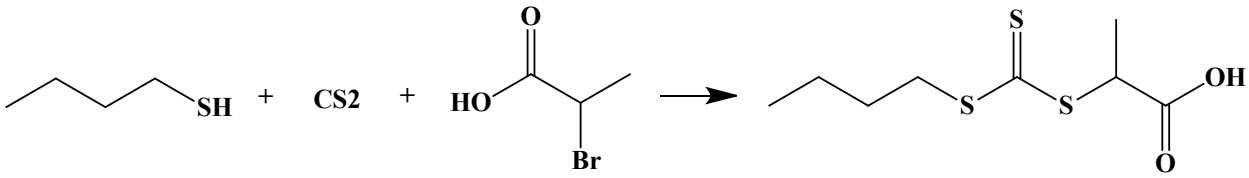


Figure S1. [1]HNMR of CEA.

b) Synthesis of a RAFT agent of 3-(benzylthiocarbonothioylthio)propanoic acid (BTPA)

Scheme S-2 Synthesis of 3-(benzylthiocarbonothioylthio)propanoic acid (BTPA).



First, 50wt% sodium hydroxide solution (NaOH, 1.03 g and distilled water 1.03ml) in 3-neck flask was prepared. After dissolve complete, added butanethiol 2.25 g (2.68 ml, 25 mmol) and acetone 2 ml, distilled water 3.75ml as additional solvent. With stirring continues 30 min after, carbon disulfide 1.69 ml(2.1 g, 28 mmol) added in ice bath to keep temperature 10° C below. After 30 min, wait to synthesis temperature back to the room temperature (not heat), then added 2-bromopropanoic acid 2.3 ml (3.92g, 25.6mmol) with reaction temperature keep 30 ° C below condition. And using dropping funnel, NaOH 50 wt% aqueous solution 2 g dropped slowly by dropping funnel for 30 min. After exotherm stopped, ice bath removed then added distilled water 3.75 ml. Reaction continue to 24 hour under room temperature. After 24 hour, the solution dilute step proceed with added distilled water 6.25 ml. Then isolated and added 11.2 M HCl 4~5 ml with ice bath for keep temperature 10 ° C below. Then yellow

solid was collected used acid for precipitation then filtered and stirred in distilled water (cold temperater) for 15 min. Collected filtered yellow solid wash with cold distilled water and dry using vacuum method. After vacuum dried yellow soild dissolved in hexane 11.25 ml at 40 ° C then recrystallized with fridge then filtered. With this cycle proceed several times for purification.

Yield 3.17 g , 38.3 %

b-1) NMR peak of BTPA's

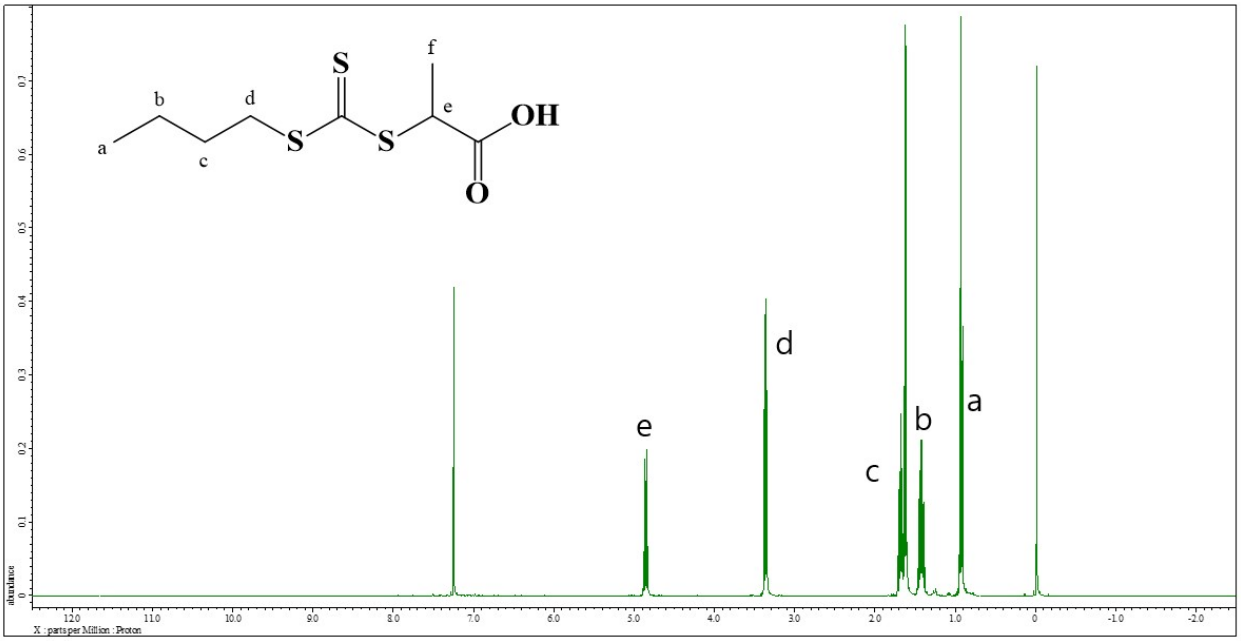


Figure S2. [1]HNMR of BTPA

2. Physical properties of hydrogels

a) Young's modulus, crosslinking density calculation at angular frequency 1 by under table conclusions

Table S1. Frequency sweep analysis for Storage modulus, Loss modulus, Young's modulus, Crosslink density and Tangent delta of PET-RAFT & Orthogonal reaction hydrogel (at angular frequency at 1)

Sample name	Storage Shear Modulus (Pa)	Young's Modulus (Pa)*	Loss Shear Modulus (Pa)	Crosslink Density (mole/m^3)	Tangent delta
G15B0	16900	50721	473	2.27	0.028
G15B1	18000	54147	1330	2.42	0.074
G15B3	19400	58584	2230	2.61	0.115
G15B5	22100	66375	1050	2.97	0.048
G15B10	22000	66048	826	2.96	0.038
G15B15	22000	66105	1250	2.96	0.057
G15B30	22200	66957	2300	2.99	0.104

***Young's modulus can be calculated with 3 times shear modulus approximately.**

Following these equations under blow

E(Young's modulus)=2G(1+v)

G(Shear modulus), v(Poisson's ratio ~1)

$$E^{'}(Storage\ Modulus) = 3\rho RT$$

(ρ=Crosslink Density, R=Gas constan, 8.314 J·mol^{-1}·K^{-1}t and T=Absolute temperature, 298K)

$$E(Shear\ modulus) = E^{'}(Storage\ Modulus) + iE^{''}(LossModulus)$$

$$Tangent\ delta = \frac{Loss\ modulus}{Storage\ modulus}$$

b) SEM image about hydrogel samples after freeze dry.

The prepared hydrogels were measured by field emission scanning electron microscopy (FE-SEM, SU8000)

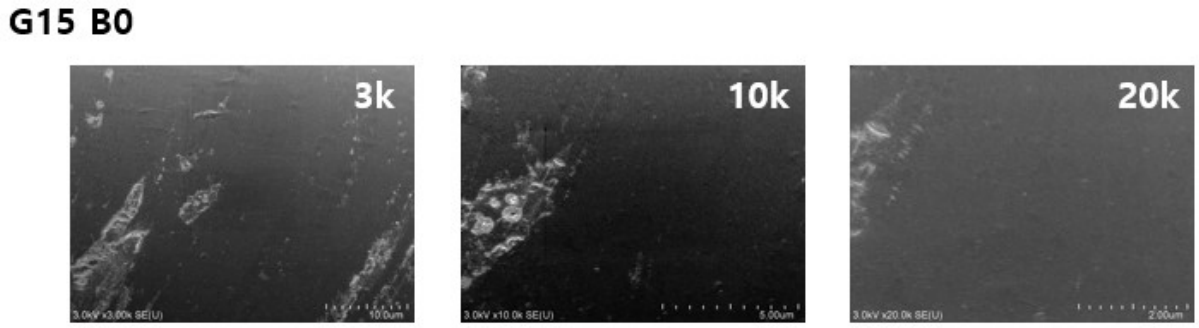


Figure S3. SEM micrographs o f **G15BO**.

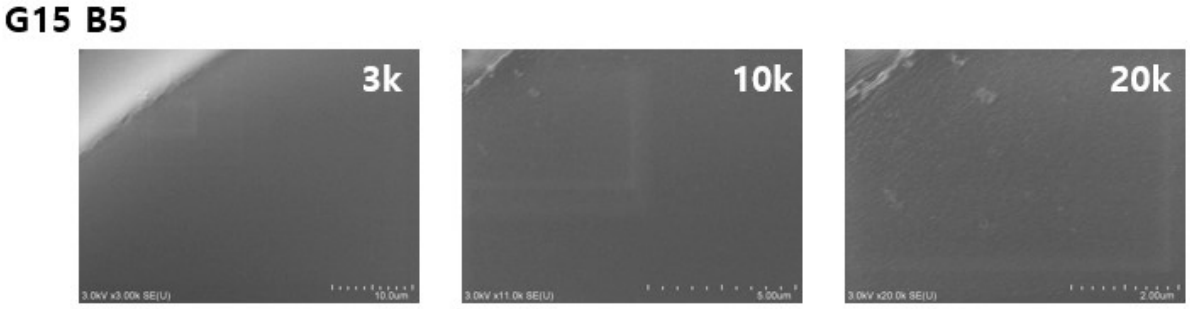


Figure S4. SEM micrographs o f **G15BB5**.

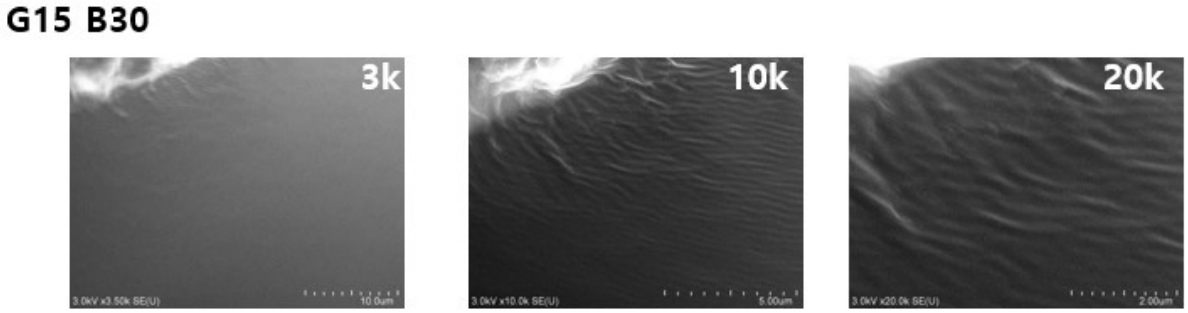


Figure S5. SEM micrographs o f **G15BB30.**

h) Differential Scanning Calorimetry (DSC) analysis

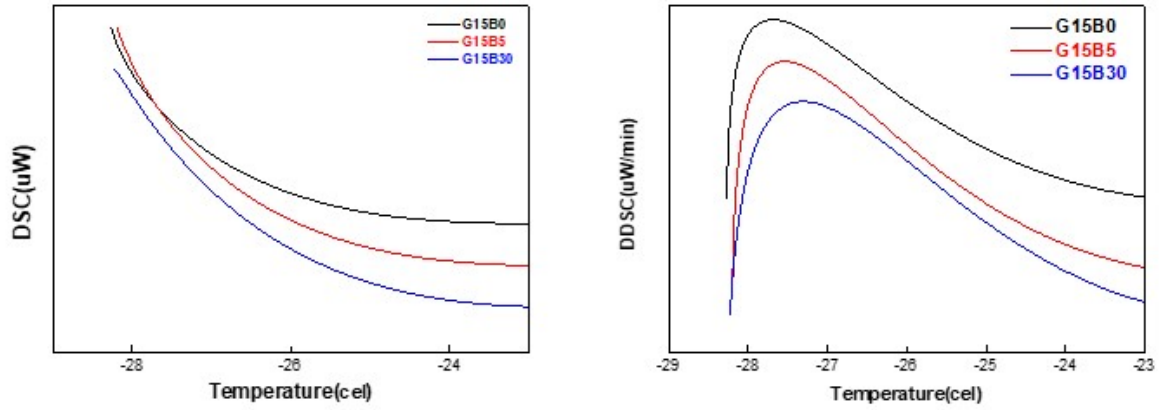


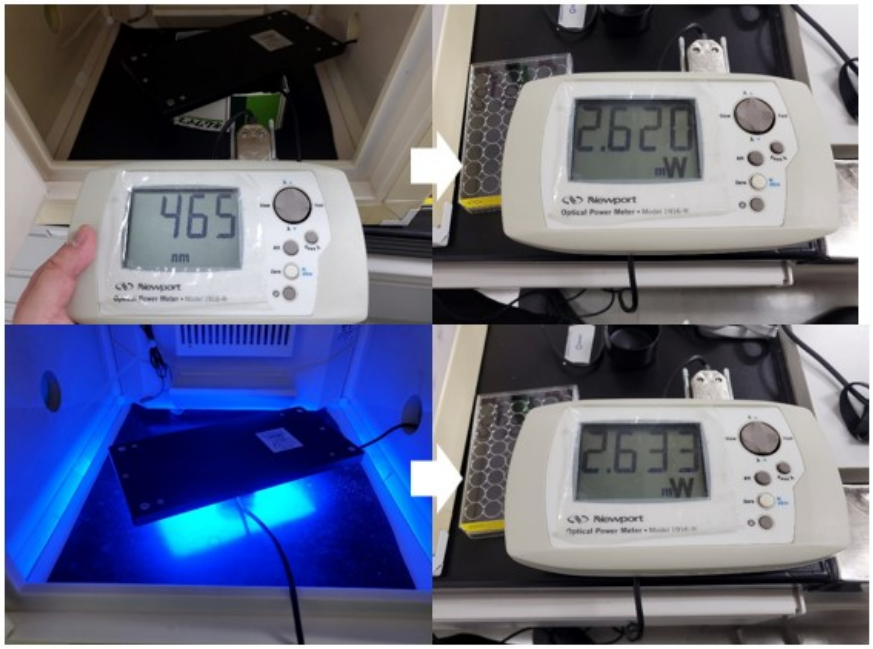
Figure S6. Thermal analysis of the hydrogels.

Table S2 Glass transition temperature (Tg) of the hydrogels.

	Tg (˚C)
G15B0	27.68
G15B5	27.53
G15B30	27.14

3. Experimental conditions.

a) Light intensity of LED.



Blue light intensity area 2.620mW to 2.633mW.

Green light intensity area 1.421mW to 1.451mW.

(All of sample analysis of light intensity have condition about distance to detector that 5cm to 0cm.)

b) Definition of bending angle

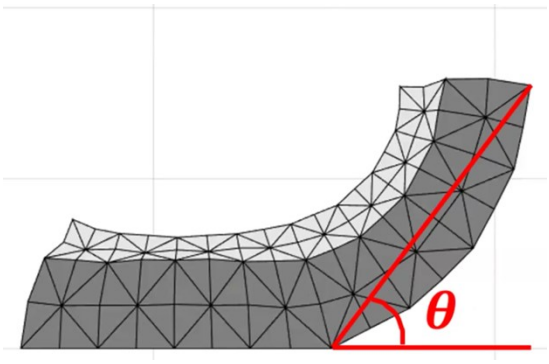


Figure S7. Definition of bending angle of hydrogel.