# **Supporting Information**

Preparation of cross-linked poly(vinyl alcohol) films via copolymers with benzoxaborole and carboxylic acid groups, and their degradability in an oxidizing environment

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### 1. Experimental methods

#### 1.1. Materials

Five-methacrylamido-1,2-benzoxaborole (MAAmBO) was synthesized and purified according to the previous protocol.<sup>1,2</sup> Methacrylic acid (MAAc) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and purified by passing through basic alumina column. Poly(vinyl alcohol) (PVA, Mw 89,000-98,000 g/mol, 99+% hydrolyzes) was purchased from Sigma-Aldrich and was used as received. NaClO•5H<sub>2</sub>O was provided by the Nippon Light Metal Co. Ltd.(Japan). NaClO•5H<sub>2</sub>O is commercially available from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co. Ltd., and Junsei Chemical Co., Ltd. in Japan. TCI America and TCI Europe also provide NaClO•5H<sub>2</sub>O as a reagent. All other chemicals and solvents were used as received.

# 1.2. Preparation of poly(MAAc) and poly(MAAc-co-MAAmBO)s

The free radical polymerization was employed to synthesize the poly(MAAc) and poly(MAAc-*co*-MAAmBO)s. A synthesis method of poly(MAAc) is shown below. Briefly, MAAc (2.375 g, 27.6 mmol) and 4,4'-azobis-4-cyanovaleric acid (ACVA) (38.67 mg,  $1.38 \times 10^{-1}$  mmol) ([MAAc]<sub>0</sub>/[ACVA]<sub>0</sub> = 200/1) were dissolved in 10 mL of *N*, *N*-dimethylformamide (DMF). After degassing with nitrogen gas for 30 min., the solution was polymerized for 3 hours at 60 °C. The resulting poly(MAAc) was purified by dialysis against water and was dried by lyophilization. The poly(MAAc) was obtained as a white powder with 62 % yield. The molecular weight (*M*<sub>n</sub>) and molecular weight distribution (*M*<sub>w</sub>/*M*<sub>n</sub>) (measured by gel permeation chromatography (GPC)) of poly(MAAc) were 93700 g/mol and 1.90.

Poly(MAAc-*co*-MAAmBO)s were synthesized by the similar protocol. A typical synthesis method of poly(MAAc-*co*-MAAmBO\_3) (5 mol% MAAmBO in feed) is shown below. Briefly, MAAc (2.252 g, 26.2 mmol), MAAmBO (298.8 mg, 1.38 mmol) and ACVA (38.67 mg,  $1.38 \times 10^{-1}$  mmol) ([MAAc]<sub>0</sub>/[MAAmBO]<sub>0</sub>/[ACVA]<sub>0</sub> = 190/10/1) were dissolved in 10 mL of DMF. After degassing with nitrogen gas for 30 min., the

solution was polymerized for 3 hours at 60 °C. The resulting poly(MAAc-*co*-MAAmBO\_3) was purified by dialysis, firstly against ethanol/water (1/1 v/v) and then water, and was dried by lyophilization. The poly(MAAc-*co*-MAAmBO\_3) was obtained as a light brown powder with 88 % yield. The  $M_n$  and  $M_w/M_n$  of poly(MAAc-*co*-MAAmBO 3) were 60300 g/mol and 2.07.

Poly(MAAc-*co*-MAAmBO\_17) (30 mol% MAAmBO in feed) was also polymerized by the different monomer ratios. Briefly, MAAc (1.661 g, 19.3 mmol), MAAmBO (1.792 g, 8.26 mmol) and ACVA (38.67 mg,  $1.38 \times 10^{-1}$  mmol) ([MAAc]<sub>0</sub>/[MAAmBO]<sub>0</sub>/[ACVA]<sub>0</sub> = 140/60/1) were dissolved in 13 mL of DMF. After degassing with nitrogen gas for 30 min., the solution was polymerized for 21 hours at 60 °C. The resulting poly(MAAc-*co*-MAAmBO\_17) was purified by dialysis, firstly against ethanol/water (1/1 v/v) and then water, and was dried by lyophilization. The poly(MAAc-*co*-MAAmBO\_17) was obtained as a light brown powder with 67 % yield. The  $M_n$  and  $M_w/M_n$  of poly(MAAc*co*-MAAmBO\_17) were 84200 g/mol and 1.66.

# **1.3.** Preparation of thermal cross-linked PVA/poly(MAAc) and PVA/poly(MAAc*co*-MAAmBO) films

Total weight of PVA and poly(MAAc) (or poly(MAAc-*co*-MAAmBO)) was 600 mg. In the PVA/poly(MAAc) and PVA/poly(MAAc-*co*-MAAmBO\_3) films, the polymers were dissolved in 10 mL water at the 10 wt% of poly(MAAc) (or poly(MAAc-*co*-MAAmBO)) content (*i.e.* PVA/poly(MAAc) = 540/60 mg). Each mixed solution was displaced to a 55 mm plastic dish, and was dried at 40 °C oven (1 day) and under reduced pressure (1 day). The PVA/poly(MAAc-*co*-MAAmBO\_3) films were also prepared at different poly(MAAc-*co*-MAAmBO\_3) contents (5 and 20 wt%). The films were cross-linked at 135 °C oven at different thermal crosslinking times (40 min., 2 hours, and 4 hours). In the PVA/poly(MAAc-*co*-MAAmBO\_17) films, the polymers (total 600 mg) were dissolved in 15 mL ethanol/water (1/1 wt) at the 10 wt% of poly(MAAc-*co*-MAAmBO\_17) content. The mixed solution was displaced to a 55 mm plastic dish, and was dried at 40 °C oven (1 day) and under reduced pressure (1 day). The films were cross-linked at 135 °C oven at different thermal crosslinking times (40 a 55 mm min., 2 hours, and 4 hours).

# 1.4. Degradable tests of thermal cross-linked PVA/poly(MAAc) and PVA/poly(MAAc-*co*-MAAmBO) films in an oxidation environment of the sodium hypochlorite pentahydrate (NaClO•5H<sub>2</sub>O) aqueous solution

Thermal crosslinked (at 135 °C for 4 hours) PVA/poly(MAAc), PVA/poly(MAAc-*co*-MAAmBO\_3), PVA/poly(MAAc-*co*-MAAmBO\_17) films were immersed for degradable tests in an oxidation environment of the sodium hypochlorite pentahydrate (NaClO•5H<sub>2</sub>O) aqueous solution. Polymeric films were cut (around 5~10 mg) as a square sample and were added to the NaClO•5H<sub>2</sub>O aqueous solution (12 mg NaClO•5H<sub>2</sub>O /mL) to be the same concentration (0.1 wt %, *e.g.*, 10 mg of film sample was added to 10 mL NaClO•5H<sub>2</sub>O aqueous solution). The molar ratio of PVA unit of the film and NaClO•5H<sub>2</sub>O was adjusted at 1/3.6 (*i.e.* surplus NaClO•5H<sub>2</sub>O against PVA units). After the degradable tests at different time (5, 25, and 50 hours), all films were washed with water and were dried under atmospheric pressure. The residual weights of the films were measured using 3 different samples (N = 3).

# **1.5.** Stability tests of PVA/poly(MAAc) and PVA/poly(MAAc-*co*-MAAmBO) films in hot water before/after thermal crosslinking

PVA/poly(MAAc), PVA/poly(MAAc-co-MAAmBO 3), PVA/poly(MAAc-co-MAAmBO 17) films before/after thermal crosslinking were immersed for stability tests in hot water (80 °C). Polymeric films were cut (around 5 mm<sup>2</sup>) as a square sample and were added to a large amount of water (1.5 mL, 80 °C). After 3 hours, all films were washed with water and were dried under atmospheric pressure. Polymeric films were measured using 3 different samples (N = 3). The residual weights were calculated using numerical expression: (dry-weight after immersion/dry-weight the before immersion)\*100. The swelling ratios were calculated using the numerical expression: swelling-film immersion(mm<sup>2</sup>)/area (area of after of dry-film before

immersion(mm<sup>2</sup>))\*100. The water contents were calculated using the numerical expression: (water weight of film after immersion/dry-weight of film before immersion)\*100.

## 1.6. Characterizations

<sup>1</sup>H NMR spectra of copolymers were taken with a JNM-GSX300 spectrometer operating at 300 MHz (JEOL, Tokyo, Japan) to confirm successful synthesis and determine the chemical composition of the synthesized copolymers.

Molecular weight and polydispersity of the synthesized copolymers were determined by gel permeation chromatography (GPC) at 40 °C (0.2M phosphate buffer at pH 8, containing 10 vol% acetenitrile, 0.7 mL/min) with Shodex SB-802.5 HQ and Shodex SB-804 HQ columns (Showa Denko K. K., Tokyo, Japan) and connected to a RID-20A refractive index detector (Shimadzu Co., Kyoto, Japan). Poly(ethylene oxide)/poly(ethylene glycol) were used as the standard samples to make the calibration curve. The MAAmBO groups of /poly(MAAc-*co*-MAAmBO)s were covered with 1,4butanediol.<sup>3</sup>

Infrared spectra were carried out using a Fourier transform infrared spectroscopy (FT-IR) FT-IR-6100 (JASCO Co., Tokyo, Japan) with attenuated total reflectance mode (ATR). A range of wavenumber from 4000-650 cm<sup>-1</sup> and accumulation of 128 scans were used each sample.

The mechanical properties of the polymeric films were measured using a tensile testing machine AG-X plus 50 kN (Shimadzu Co., Kyoto, Japan). All films were prepared as the sample of 1cm\*5cm film. The tensile speed was 5 mm/min. (N = 3).

The thermal properties of the polymeric films were measured using a differential scanning calorimeter (DSC) DSC-60Plus (Shimadzu Co., Kyoto, Japan). Each sample was analyzed at a heating rate of 10 °C/min. The second scan results were used as the thermal properties.

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(2) Kotsuchibashi, Y.; Ebara, M.; Sato, T.; Wang, Y.; Rajender, R.; Hall, D. G.; Narain, R.; Aoyagi, T. Spatiotemporal control of synergistic gel disintegration consisting of boroxole- and glyco-based polymers via photoinduced proton transfer. *J. Phys. Chem. B* **2015**, *119*, 2323-2329.

(3) Wang, Y.; Kotsuchibashi, Y.; Uto, K.; Ebara, M.; Aoyagi, T.; Liu, Y.; Narain, R. pH and glucose responsive nanofibers for the reversible capture and release of lectins. *Biomater. Sci.* **2015**, *3*, 152-162.



Figure S1. <sup>1</sup>H NMR of copolymers in DMSO.



Figure S2.  $M_n$  and  $M_w/M_n$  of PVA in NaClO•5H<sub>2</sub>O aqueous solution at 25 °C. The weight ratio PVA:NaClO•5H<sub>2</sub>O = 1:1. The GPC solvent was PBS buffer at pH 8.



Figure S3.  $M_n$  and  $M_w/M_n$  of poly(MAAm-*co*-MAAmBO\_3) in NaClO•5H<sub>2</sub>O aqueous solution at 25 °C. The weight ratio poly(MAAm-*co*-MAAmBO\_3): NaClO•5H<sub>2</sub>O = 1:1. The GPC solvent was PBS buffer at pH 8. The MAAmBO groups were covered with 1,4-butanediol.



Figure S4. <sup>1</sup>H NMR of 2,4-pentandiol with NaClO•5H<sub>2</sub>O in D<sub>2</sub>O. The molar ratio 2,4-pentandiol/NaClO•5H<sub>2</sub>O = 1:5.



Figure S5. FT-IR spectra of (A) before and (B) after cross-linked films for 4hours. (i) PVA, (ii) PVA/poly(MAAc), (iii) PVA/poly(MAAc-*co*-MAAmBO\_3), (iv) PVA/poly(MAAc-*co*-MAAmBO\_17) films.



Figure S6. Maximum force of the PVA and PVA/benzoxaborole-based copolymer films (A) before and (B) after thermal cross-linking (CL: cross-linking).



Figure S7. Water contents of (A) PVA/poly(MAAc), (B) PVA/poly(MAAc-*co*-MAAmBO\_3), and (C) PVA/poly(MAAc-*co*-MAAmBO\_17) films. The films were immersed in 80 °C water for 3 hours. The water contents were calculated using the numerical expression: (water weight of film after immersion (g)/dry-weight of film before immersion (g))\*100.



Figure S8. Residual weights and swelling ratios of PVA/poly(MAAc-*co*-MAAmBO\_3) films at different mixture ratios with PVA. The films were immersed in 80 °C water for 3 hours. The residual weights were calculated using the numerical expression: (dry-

weight after immersion/dry-weight before immersion)\*100. The swelling ratios were calculated using the numerical expression: (area of swelling-film after immersion( $mm^2$ )/area of dry-film before immersion( $mm^2$ ))\*100.



Figure S9. Water contents of PVA/poly(MAAc-co-MAAmBO\_3) films at different

mixture ratios with PVA. The films were immersed in 80 °C water for 3 hours. The water contents were calculated using the numerical expression: (water weight of film after immersion/dry-weight of film before immersion)\*100.