Supporting Information

for

Supramacromolecular Injectable Hydrogels by

Crystallization-driven Self-assembly of Carbohydrate-

conjugated Poly(2-isopropylloxazoline)s for Biomedical

Applications

Tomoki Nishimura*, Naoki Sumi, Sada-atsu Mukai, Yoshihiro Sasaki, Kazunari Akiyoshi*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
Fig. S1 $^1$H-NMR spectrum of peracetylated maltopentaose-conjugated poly(2-isopropylxazoline) in DMSO-$_d_6$. 
Fig. S2 $^1$H-NMR spectrum of maltopentaose-conjugated poly(2-isopropylxazoline) in DMSO-$d_6$/D$_2$O = 9/1, v/v.
Fig. S3 a) Time conversion plot of the polymerization of 2-isopropyl-2-oxazoline in the presence of peracetylated maltopentaosyl bromide and AgOTf. b) SEC curves of the polymerization samples after 5, 28, and 44 h.

- $M_n: 1.34 \times 10^4 \text{ g/mol}$
- $M_w/M_n: 1.09$
Fig. S4 a) SEC curve and b) $^1$H-NMR spectrum of peracetylated maltotriose-conjugated poly(2-isopropyloxazoline) in DMSO-$d_6$/D$_2$O = 9/1, v/v.
Fig. S5 a) SEC curve and b) $^1$H-NMR spectrum of peracetylated glucose-conjugated poly(2-isopropylxazoline) in DMSO-$d_6$/D$_2$O = 9/1, v/v.
Fig. S6 The transmittance change at 500 nm of a solution of a) maltopentaose-conjugated poly(2-isopropyloxazoline), b) maltotriose-conjugated poly(2-isopropyloxazoline), c) glucose-conjugated poly(2-isopropyloxazoline) upon heating; [polymer]=10 mg/mL; heating rate = 1 K/min.
Fig. S7 Size distribution of a self-assembled maltopentaose-conjugated poly(2-isopropoxyazoline) solution (0.5 mg/mL) in water after 1 h of incubation at 70 °C.
Fig. S8 TEM images, with negative staining using 1 wt % phosphotungstic acid solution, of a self-assembled maltopentaose-conjugated poly(2-isopropylloxazoline) (0.5 mg/mL) in water after 1 h of incubation at 70 ºC.
Fig. S9 TEM images of a self-assembled maltotriose-conjugated poly(2-isopropyloxazoline) (0.5 mg/mL) in water after different incubation time intervals; scale bar = 5 µm.
Fig. S10 TEM images of a self-assembled glucose-conjugated poly(2-isopropyloxazoline) (0.5 mg/mL) in water after different incubation time intervals; scale bar = 5 µm.
Fig. S11 a–f) TEM images of a self-assembled poly(2-isopropylazoline) (0.5 mg/mL) in water after different incubation time intervals. g) SEM image of a self-assembled poly(2-isopropylazoline) (0.5 mg/mL) in water after 48 h of incubation at 70 °C; scale bar = 5 μm.
Fig. S12 WAXS profiles of a) a self-assembled maltotriose-conjugated poly(2-isopropylloxazoline), b) a glucose-conjugated poly(2-isopropylloxazoline) solution, c) a poly(2-isopropylloxazoline) solution after different incubation time intervals: [polymer] = 3 mg/mL.
Fig. S13 WAXS profiles of freeze-dried self-assembled carbohydrate-conjugated poly(2-isopropylloxazoline) and poly(2-isopropylloxazoline) samples.
Fig. S14 Photograph of a tube-inversion test of a self-assembled poly(2-isopropylloxazoline) solution, a self-assembled glucose-conjugated poly(2-isopropylloxazoline) solution (N1), a self-assembled maltotriose-conjugated poly(2-isopropylloxazoline) solution (N2), and a self-assembled maltopentaose-conjugated poly(2-isopropylloxazoline) solution (N3). [polymer] = 30 mg/mL.
Fig. S15 Photographs of tube-inversion tests for a) a self-assembled maltotriose-conjugated poly(2-isopropylxazoline) solution (N2) with different polymer concentrations, and b) a self-assembled glucose-conjugated poly(2-isopropylxazoline) solution (N1) with different polymer concentrations.
Fig. S16 Photographs of tube-inversion tests for a self-assembled maltopentaose-conjugated poly(2-isopropylloxazoline) solution (N3) after different incubation periods at 70 °C.
The $G'$ and $G''$ values of hydrogels obtained from a) glucose-conjugated poly(2-isopropylxazoline) (N1), and b) maltotriose-conjugated poly(2-isopropylxazoline) (N2) in water (3 wt %) as a function of the angular frequency ($\omega$) at a strain amplitude of $\gamma = 0.3\%$ at 25 °C.
Fig. S18 The \( G' \) and \( G'' \) values of hydrogels (3 wt\%) obtained from a) glucose-conjugated poly(2-isopropylxazoline) (N1), b) maltotriose-conjugated poly(2-isopropylxazoline) (N2), and c) maltopentaose-conjugated poly(2-isopropylxazoline) (N3) as a function of the strain amplitude (\( \gamma \)) at a frequency of 10 rad s\(^{-1}\) at 25 °C.
Fig. S19 The $G'$ and $G''$ values of hydrogels (3 wt%) obtained from a) glucose-conjugated poly(2-isopropylloxazoline) (N1), and b) maltotriose-conjugated poly(2-isopropylloxazoline) (N2) in step-strain measurements at 25 °C, which were carried out in steps of 50% and 1% oscillatory strain for three cycles.
Fig. S20 Weight changes of the hydrogels N1-N3 in a PBS buffer (pH = 7.4) at 37 °C.

Explanatory text for movie S1
A hydrogel composed of rhodamine-labelled N3 was injected via a 26-gauge syringe into water.