Supporting Information

for

Supramacromolecular Injectable Hydrogels by Crystallization-driven Self-assembly of Carbohydrate-conjugated Poly(2-isopropyloxazoline)s for Biomedical Applications

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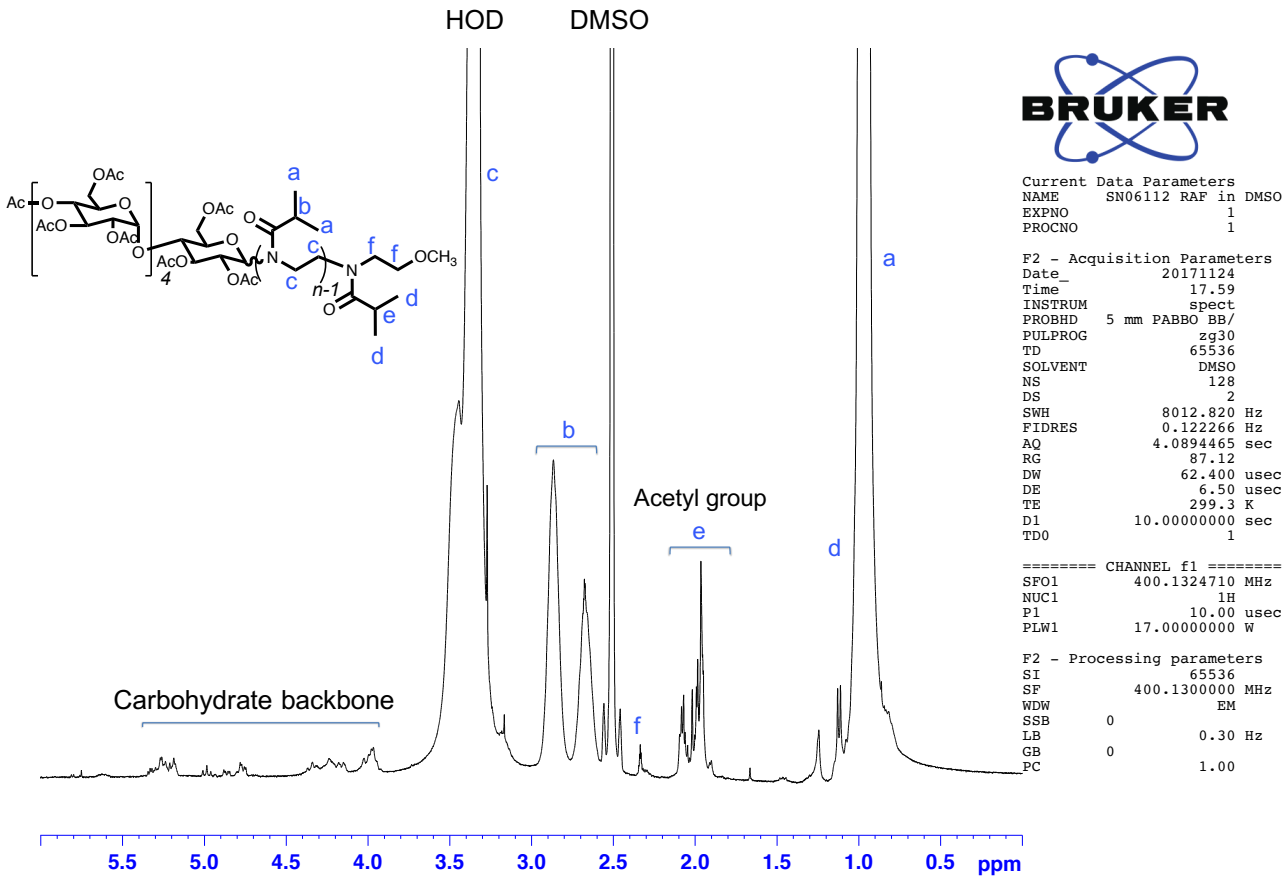
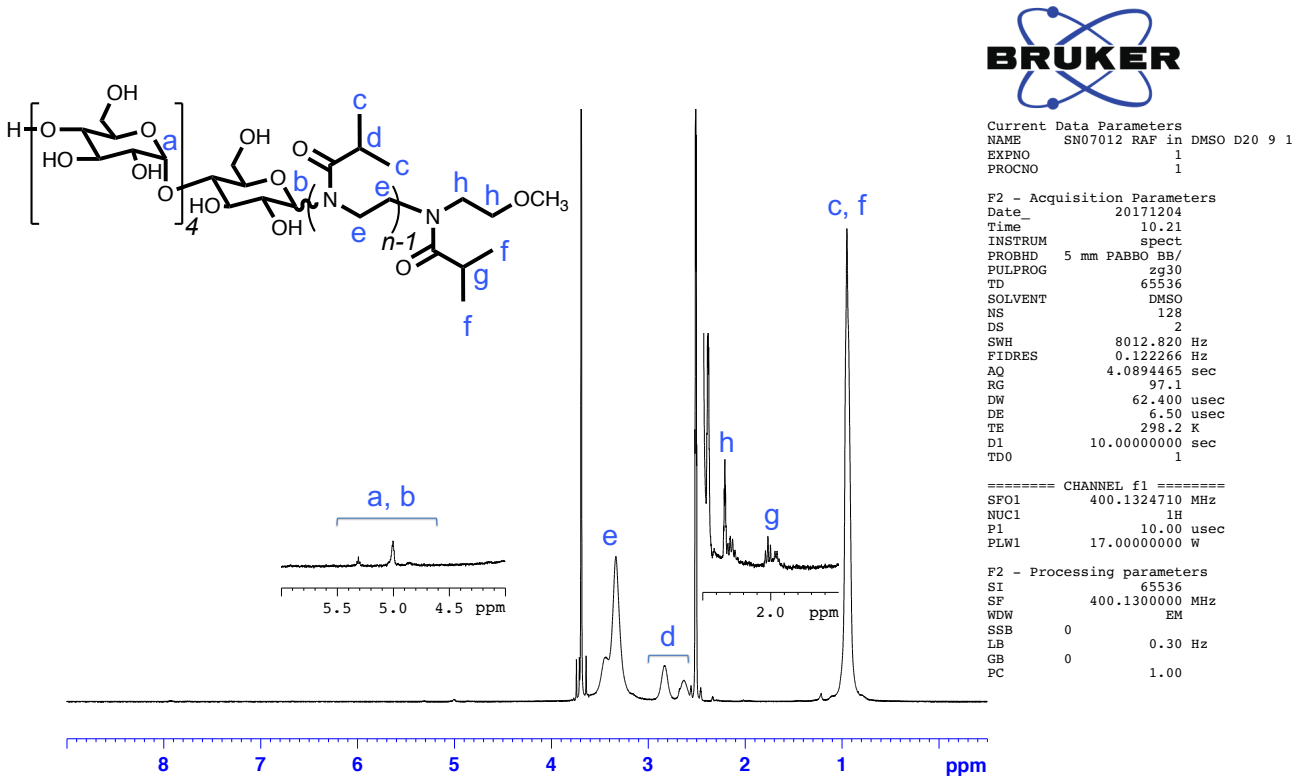


Fig. S1 ^{1}H-NMR spectrum of peracetylated maltopentaose-conjugated poly(2-isopropyloxazoline) in DMSO-d_6.



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EXPNO 1
PROCNO 1

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Time 10.21
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PULPROG zg30
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SOLVENT DMSO
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FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 97.1
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 10.00000000 sec
TD0 1

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NUC1 1H
P1 10.00 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. S2 ^{1}H-NMR spectrum of maltopentaose-conjugated poly(2-isopropyloxazoline) in DMSO-d_6/D_2O = 9/1, v/v.

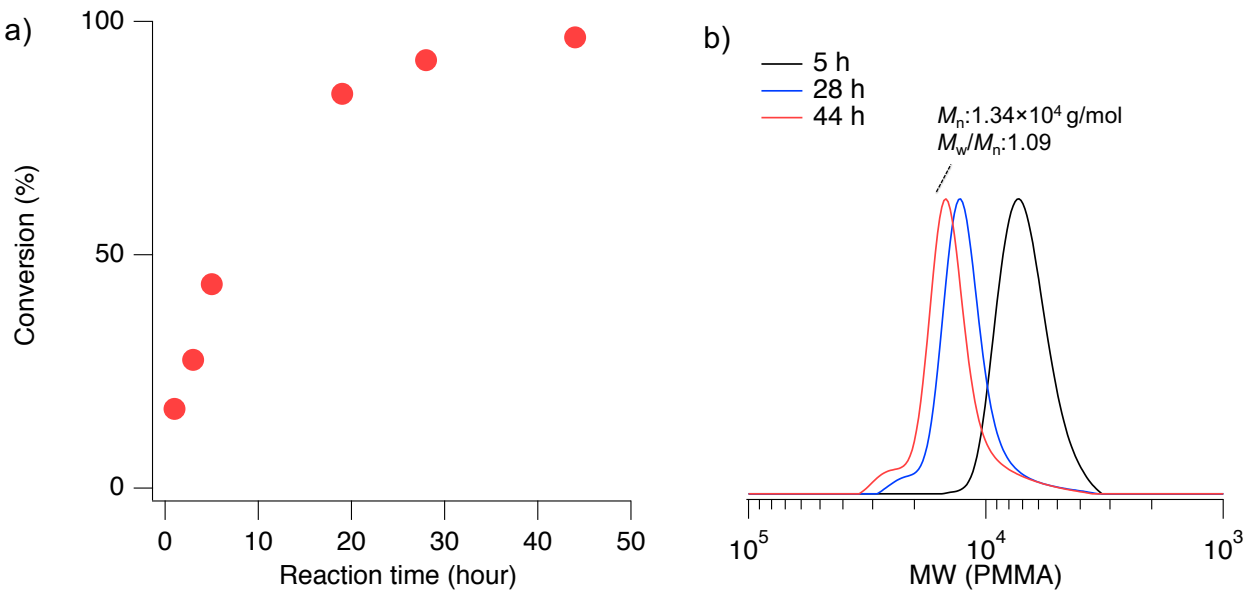

Fig. S3 a) Time conversion plot of the polymerization of 2-isopropyl-2-oxazoline in the presence of peracetylated maltopentaosyl bromide and AgOTf. b) SEC curves of the polymerization samples after 5, 28, and 44 h.

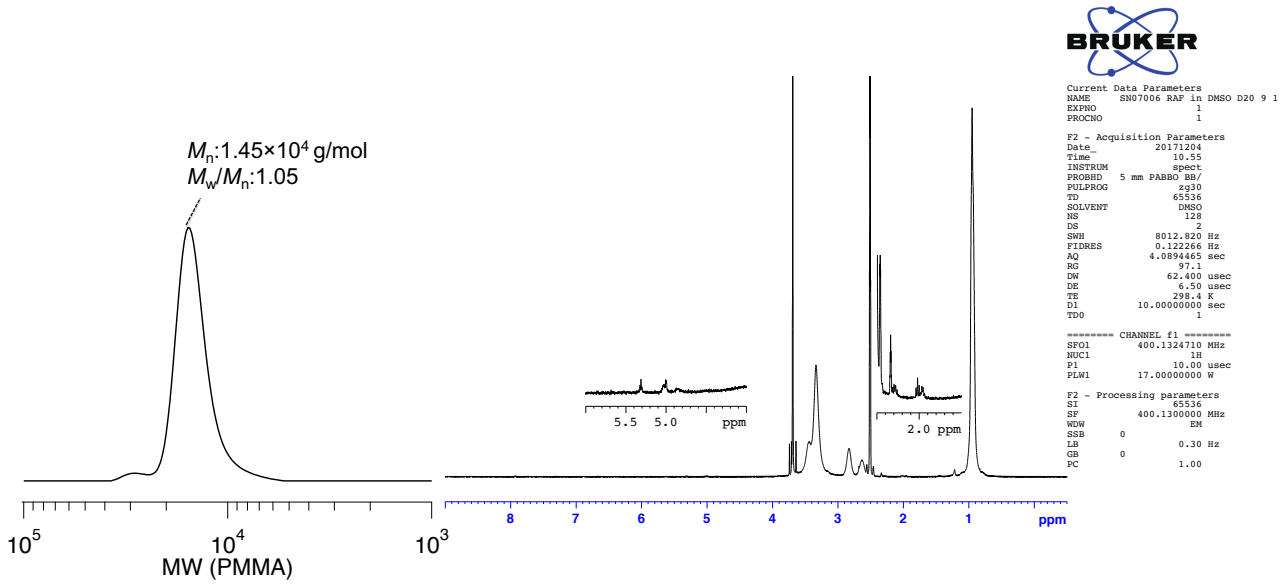

Fig. S4 a) SEC curve and b) ^{1}H-NMR spectrum of peracetylated maltotriose-conjugated poly(2-isopropyloxazoline) in in DMSO-d_6/D_2O = 9/1, v/v.

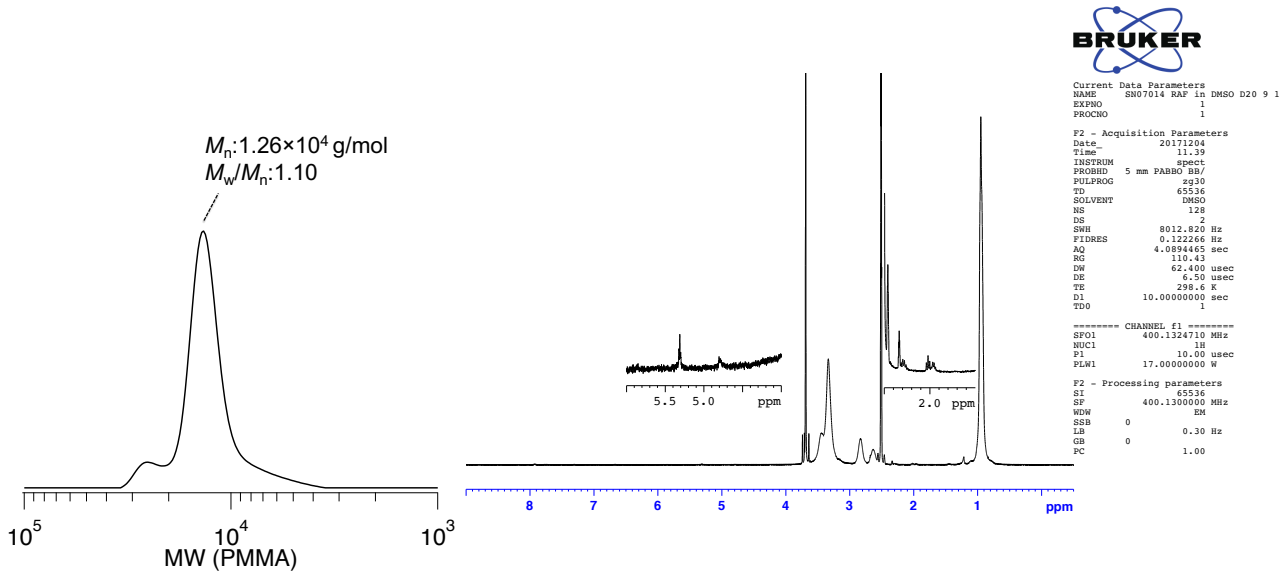

Fig. S5 a) SEC curve and b) ^{1}H-NMR spectrum of peracetylated glucose-conjugated poly(2-isopropyloxazoline) in DMSO-d_6/D_2O = 9/1, v/v.

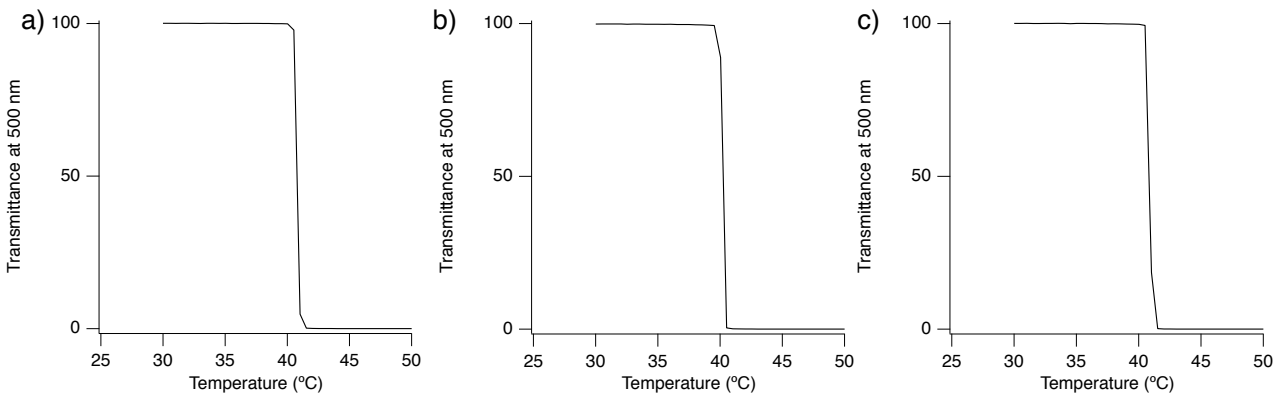

Fig. S6 The transmittance change at 500 nm of a solution of a) maltopentaose-conjugated poly(2-isopropyloxazoline), b) maltotriose-conjugated poly(2-isopropyloxazoline), c) glucose-conjugated poly(2-isopropyloxazoline) upon heating; [polymer]=10 mg/mL; heating rate = 1 K/min.

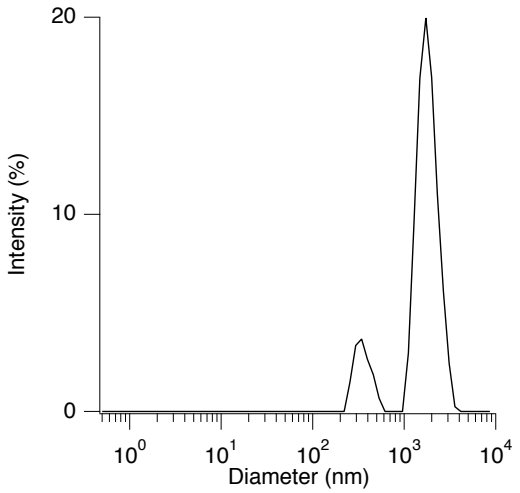

Fig. S7 Size distribution of a self-assembled maltopentaose-conjugated poly(2-isopropyloxazoline) solution (0.5 mg/mL) in water after 1 h of incubation at 70 ºC.

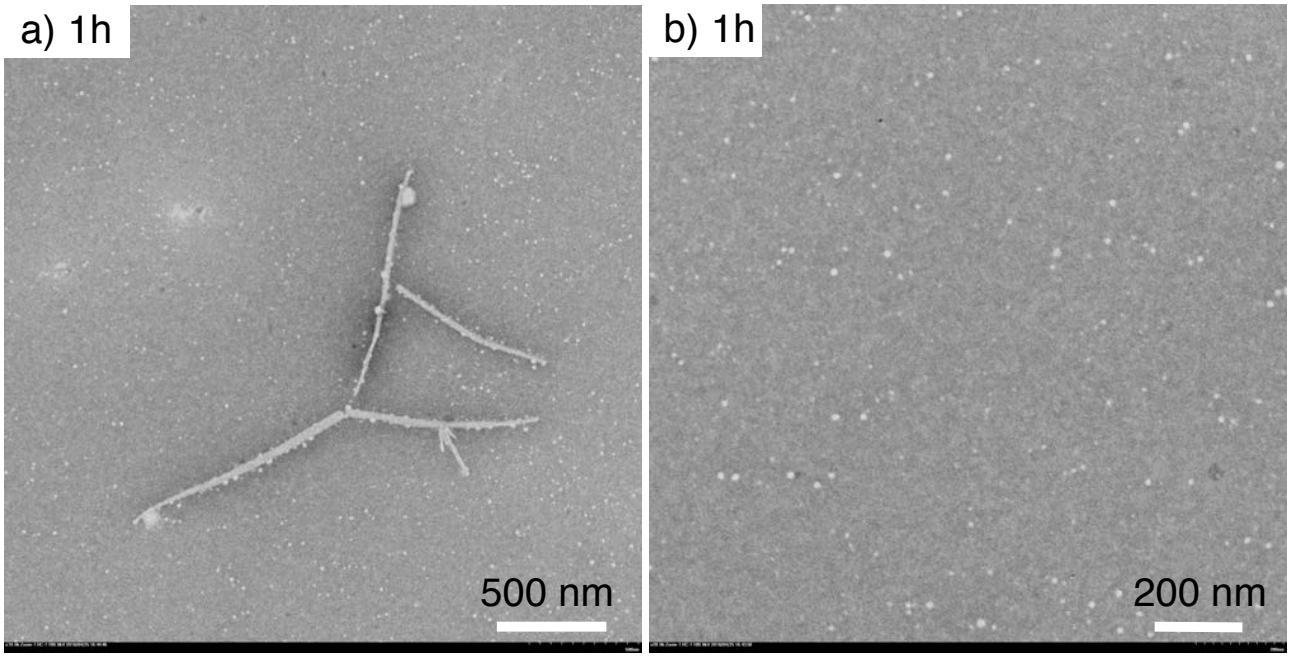

Fig. S8 TEM images, with negative staining using 1 wt % phosphotungstic acid solution, of a self-assembled maltopentaose-conjugated poly(2-isopropyloxazoline) (0.5 mg/mL) in water after 1 h of incubation at 70 ºC.

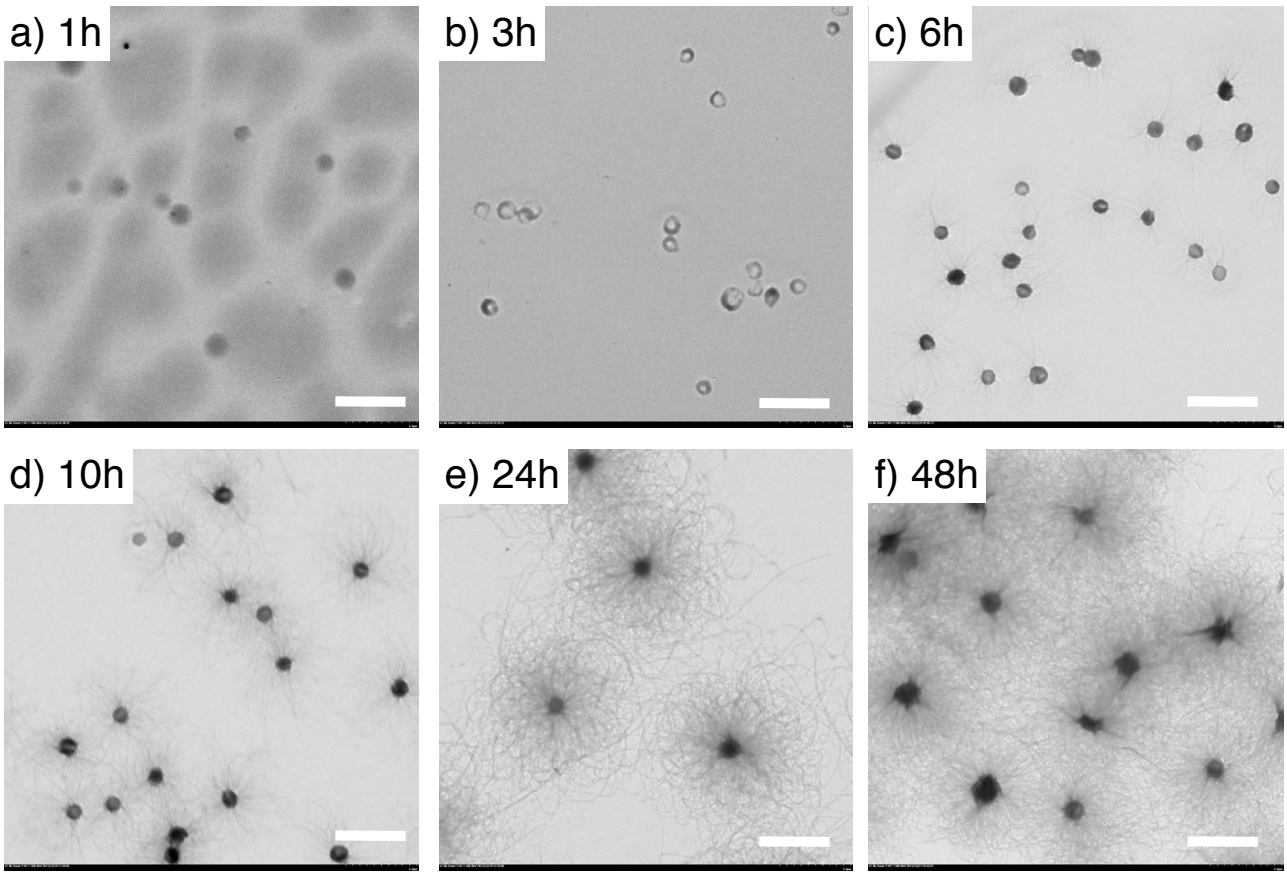

Fig. S9 TEM images of a self-assembled maltotriose-conjugated poly(2-isopropyloxazoline) (0.5 mg/mL) in water after different incubation time intervals; scale bar = 5 μm.

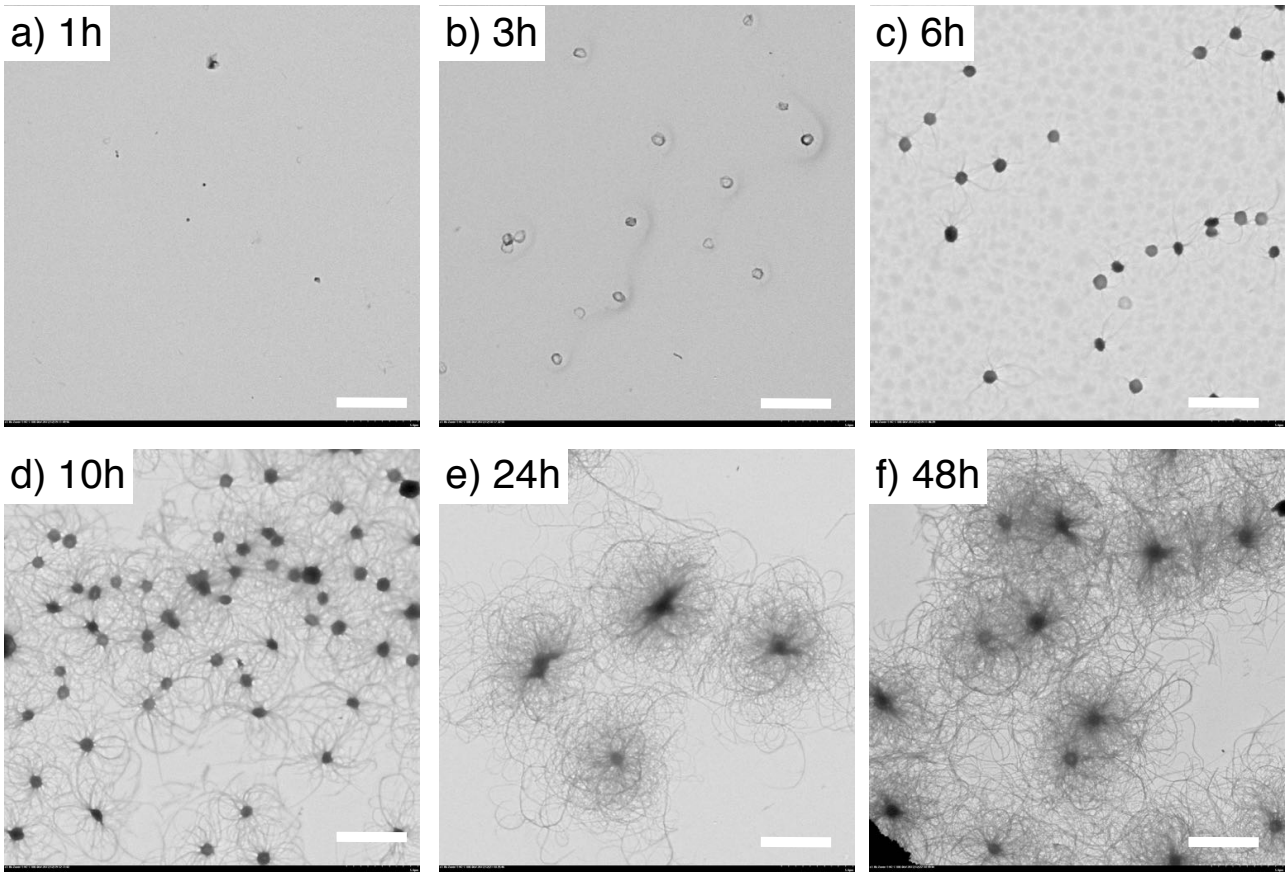

Fig. S10 TEM images of a self-assembled glucose-conjugated poly(2-isopropyloxazoline) (0.5 mg/mL) in water after different incubation time intervals; scale bar = 5 μm.

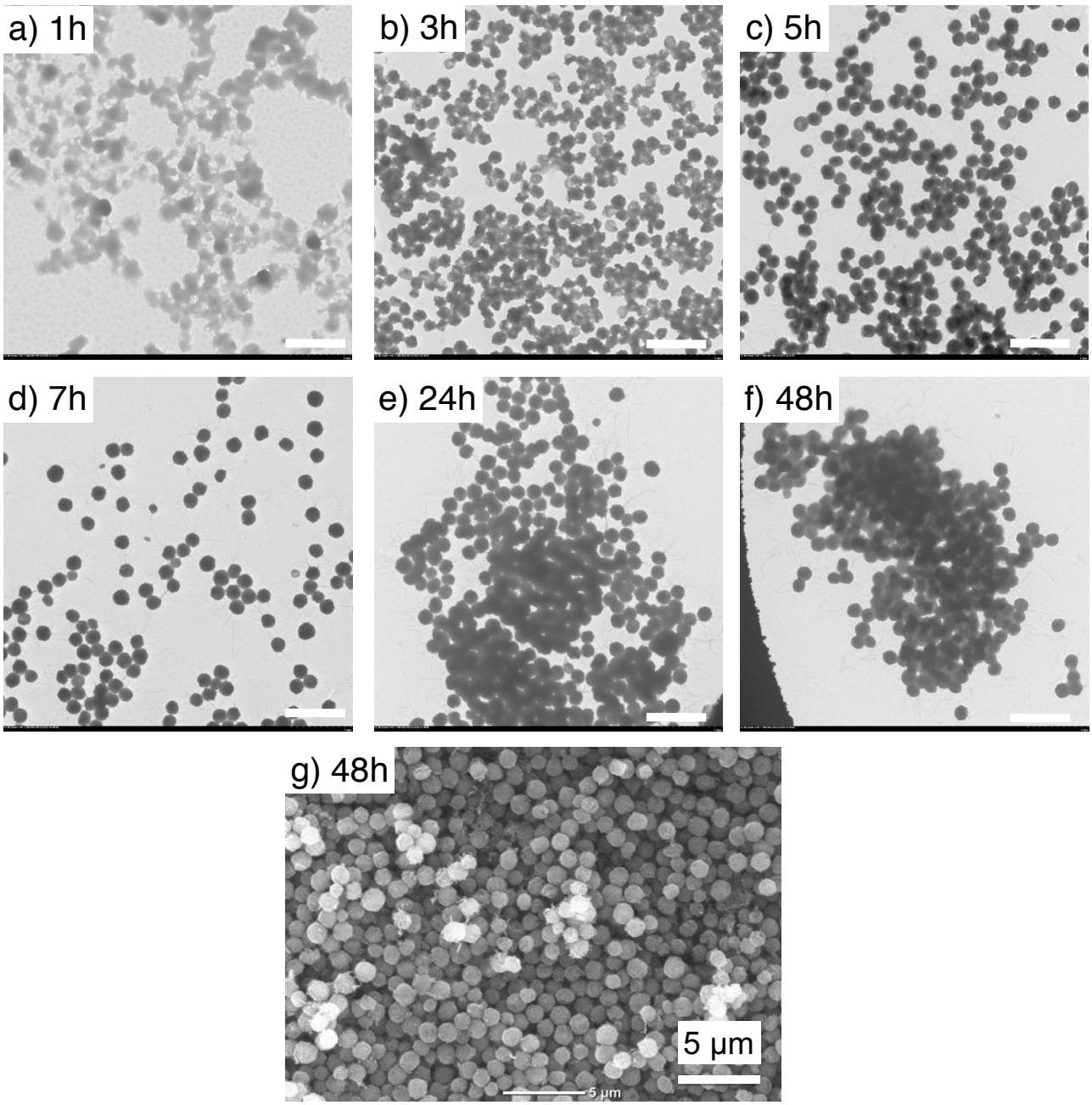

Fig. S11 a–f) TEM images of a self-assembled poly(2-isopropyloxazoline) (0.5 mg/mL) in water after different incubation time intervals. g) SEM image of a self-assembled poly(2-isopropyloxazoline) (0.5 mg/mL) in water after 48 h of incubation at 70 ºC; scale bar = 5 µm.

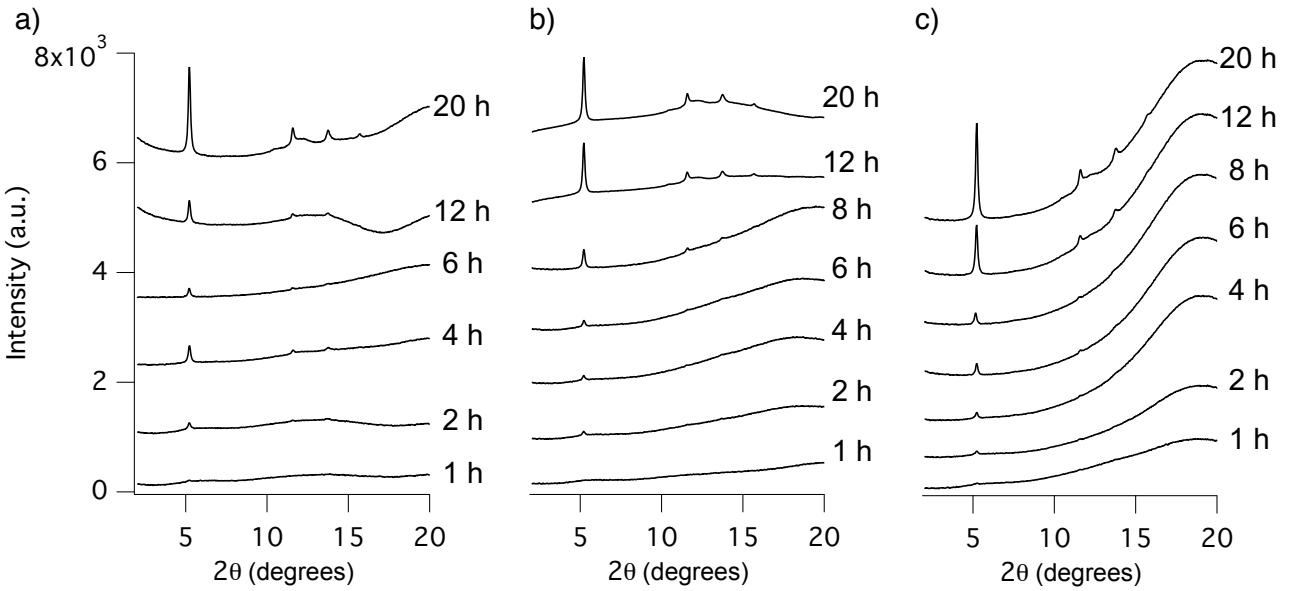

Fig. S12 WAXS profiles of a) a self-assembled maltotriose-conjugated poly(2-isopropyloxazoline), b) a glucose-conjugated poly(2-isopropyloxazoline) solution, c) a poly(2-isopropyloxazoline) solution after different incubation time intervals: [polymer] = 3 mg/mL.

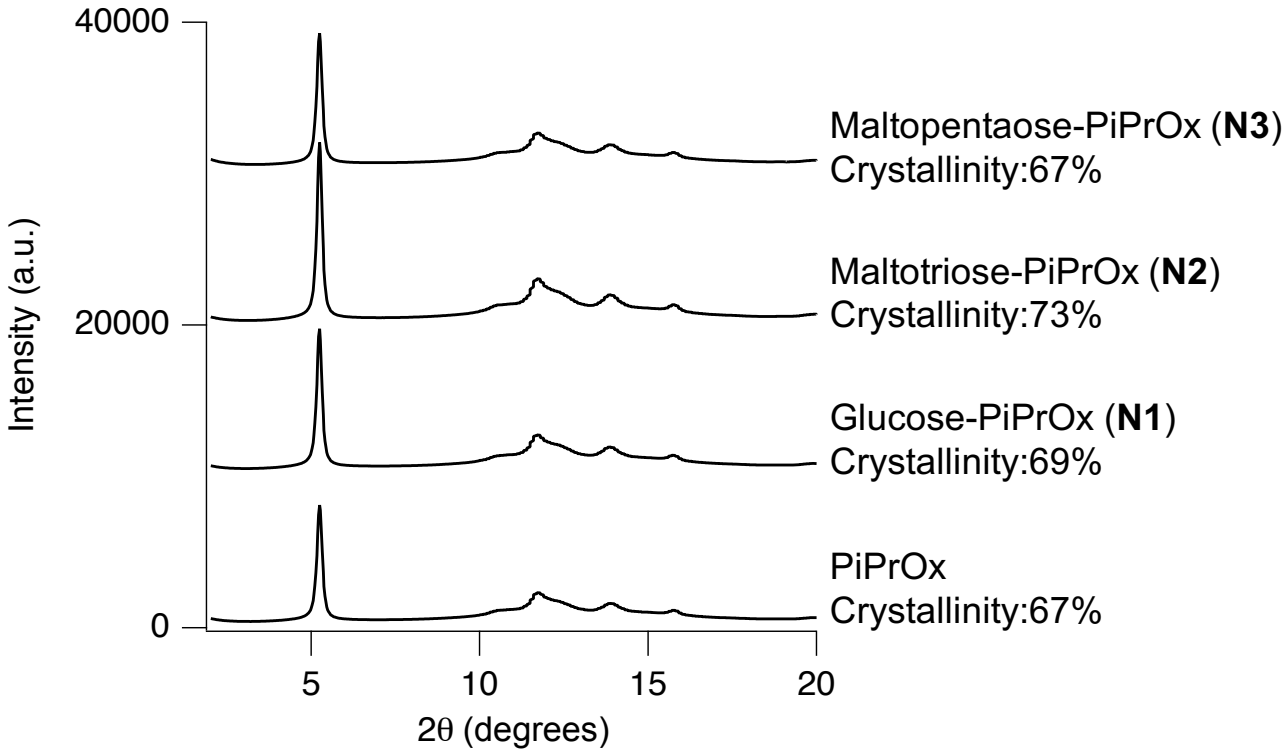

Fig. S13 WAXS profiles of freeze-dried self-assembled carbohydrate-conjugated poly(2-isopropyloxazoline) and poly(2-isopropyloxazoline) samples.

Fig. S14 Photograph of a tube-inversion test of a self-assembled poly(2-isopropyloxazoline) solution, a self-assembled glucose-conjugated poly(2-isopropyloxazoline) solution (**N1**), a self-assembled maltotriose-conjugated poly(2-isopropyloxazoline) solution (**N2**), and a self-assembled maltopentaose-conjugated poly(2-isopropyloxazoline) solution (**N3**). [polymer] = 30 mg/mL.

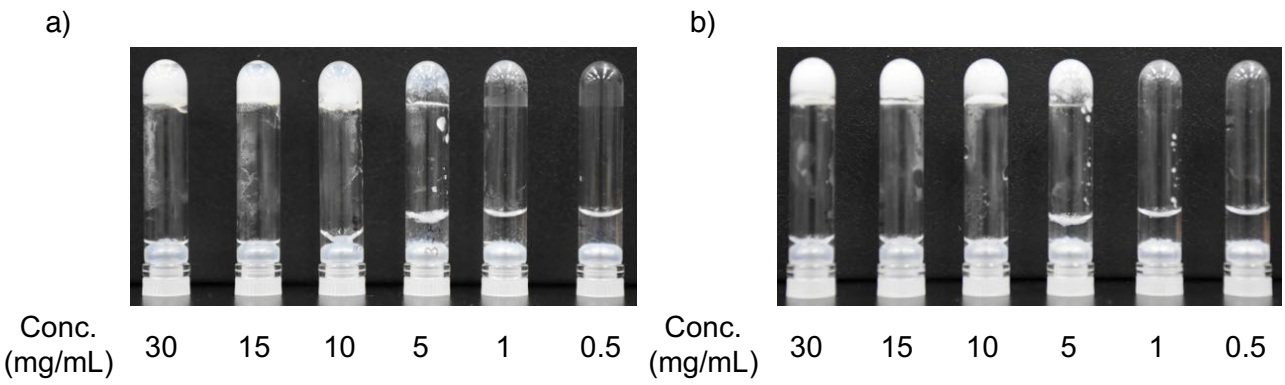

Fig. S15 Photographs of tube-inversion tests for a) a self-assembled maltotriose-conjugated poly(2-isopropyloxazoline) solution (**N2**) with different polymer concentrations, and b) a self-assembled glucose-conjugated poly(2-isopropyloxazoline) solution (**N1**) with different polymer concentrations.

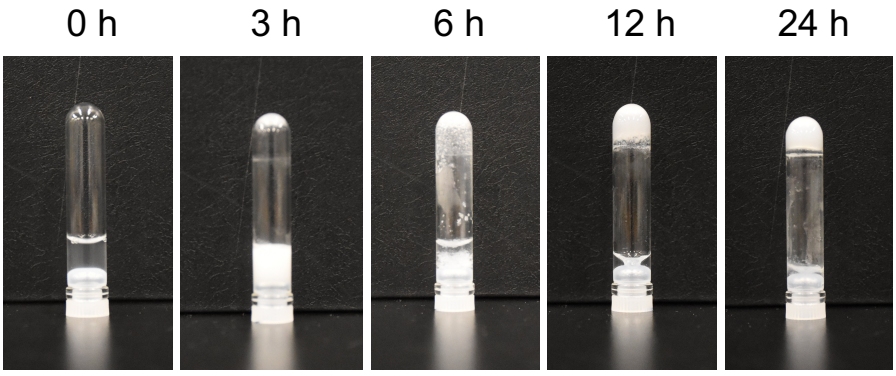

Fig. S16 Photographs of tube-inversion tests for a self-assembled maltopentaose-conjugated poly(2-isopropyloxazoline) solution (**N3**) after different incubation periods at 70 ºC.

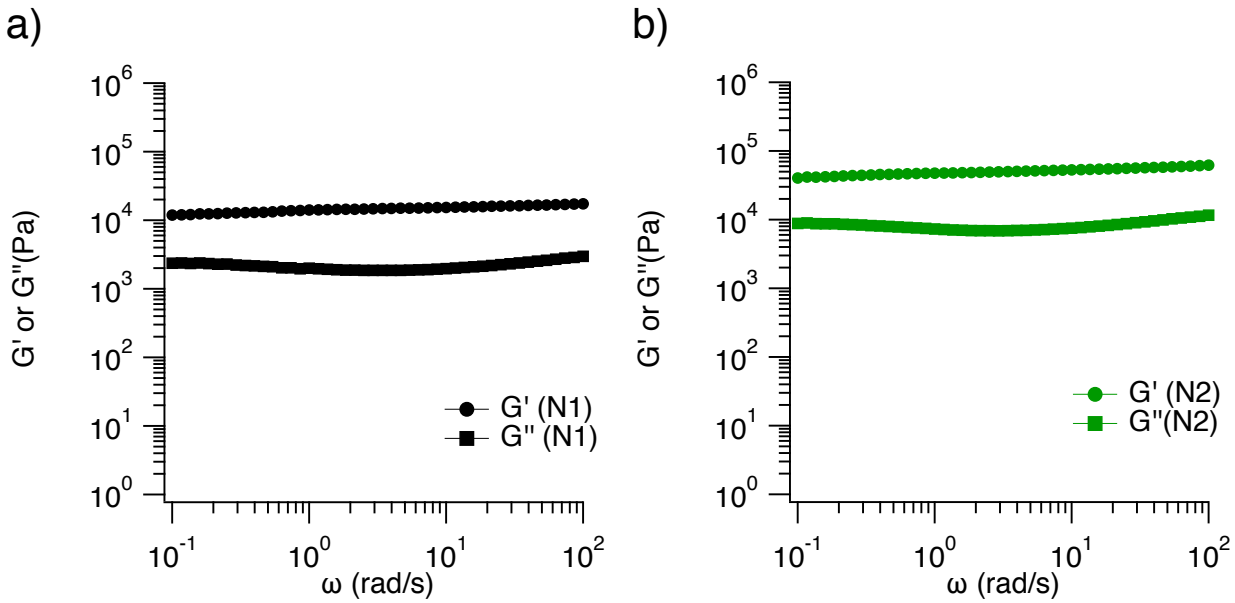

Fig. S17 The *G′* and *G″* values of hydrogels obtained from a) glucose-conjugated poly(2-isopropyloxazoline) (**N1**), and b) maltotriose-conjugated poly(2-isopropyloxazoline) (**N2**) in water (3 wt %) as a function of the angular frequency (ω) at a strain amplitude of γ = 0.3% at 25 °C.

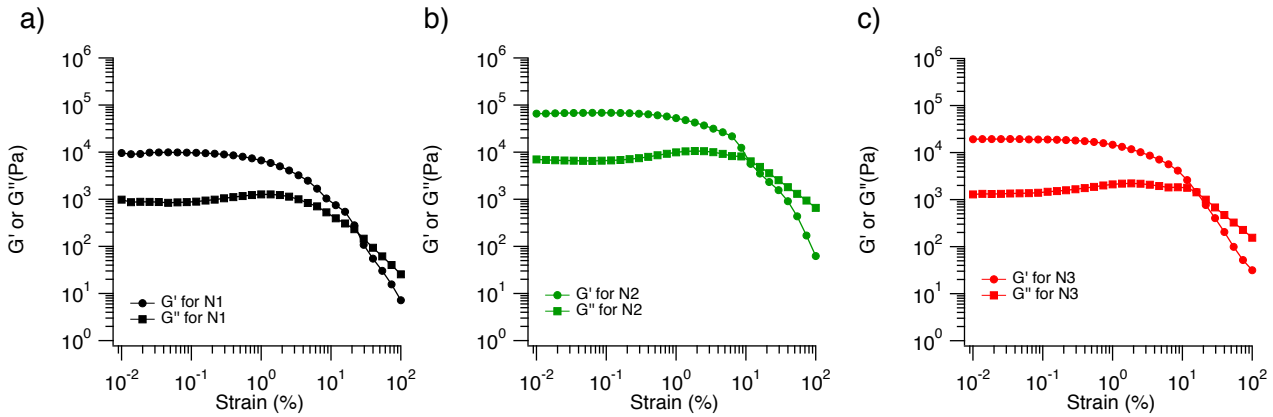

Fig. S18 The *G*' and *G*'' values of hydrogels (3 wt%) obtained from a) glucose-conjugated poly(2-isopropyloxazoline) (**N1**), b) maltotriose-conjugated poly(2-isopropyloxazoline) (**N2**), and c) maltopentaose-conjugated poly(2-isopropyloxazoline) (**N3**) as a function of the strain amplitude (γ) at a frequency of 10 rad s^{-1} at 25 ºC.

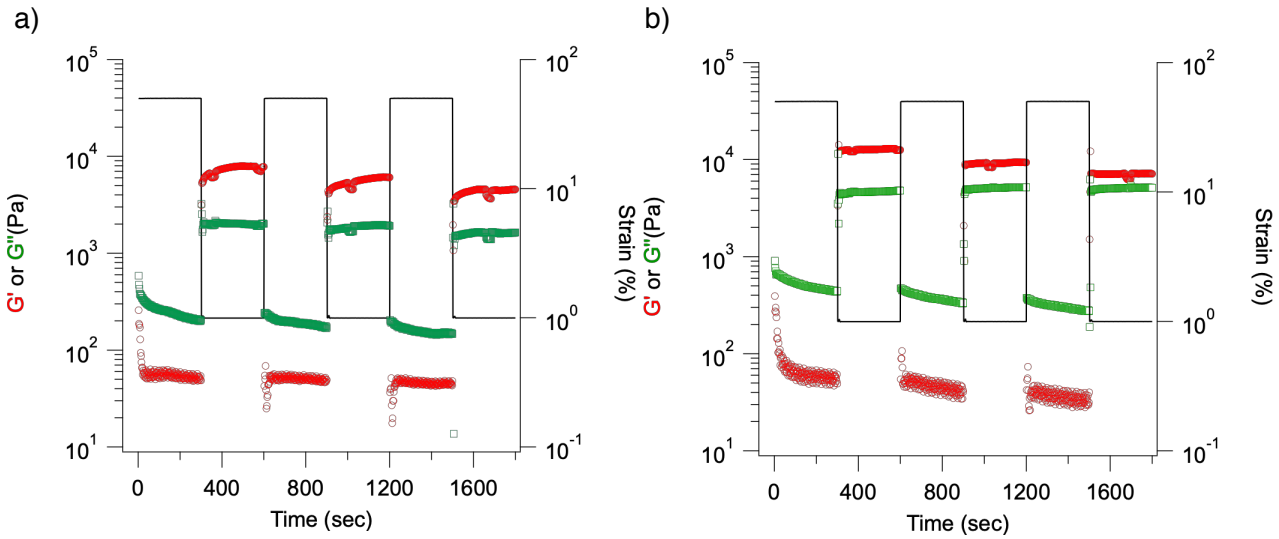

Fig. S19 The *G*' and *G*" values of hydrogels (3 wt%) obtained from a) glucose-conjugated poly(2-isopropyloxazoline) (**N1**), and b) maltotriose-conjugated poly(2-isopropyloxazoline) (**N2**) in step-strain measurements at 25 ºC, which were carried out in steps of 50% and 1% oscillatory strain for three cycles.

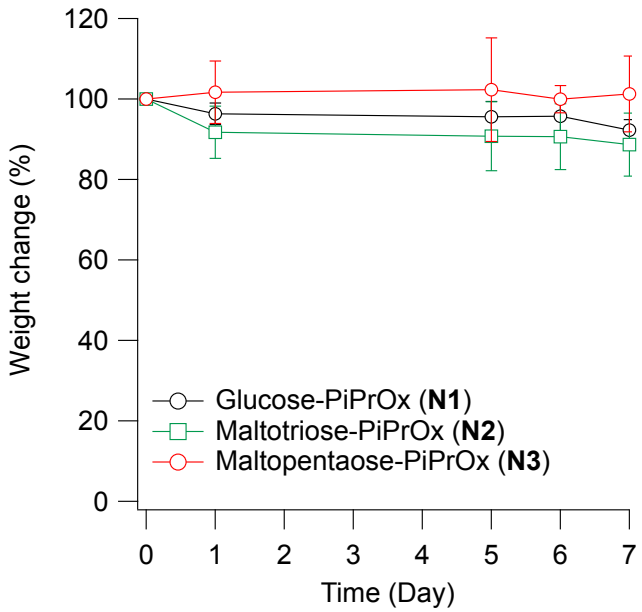

Fig. S20 Weight changes of the hydrogels **N1**-**N3** in a PBS buffer (pH = 7.4) at 37 ºC.

Explanatory text for movie S1

A hydrogel composed of rhodamine-labelled **N3** was injected *via* a 26-gause syringe into water.