Supporting information

Enzymatic conversion of galactose-polymers into copolymers containing galactonic acid by glucose oxidase

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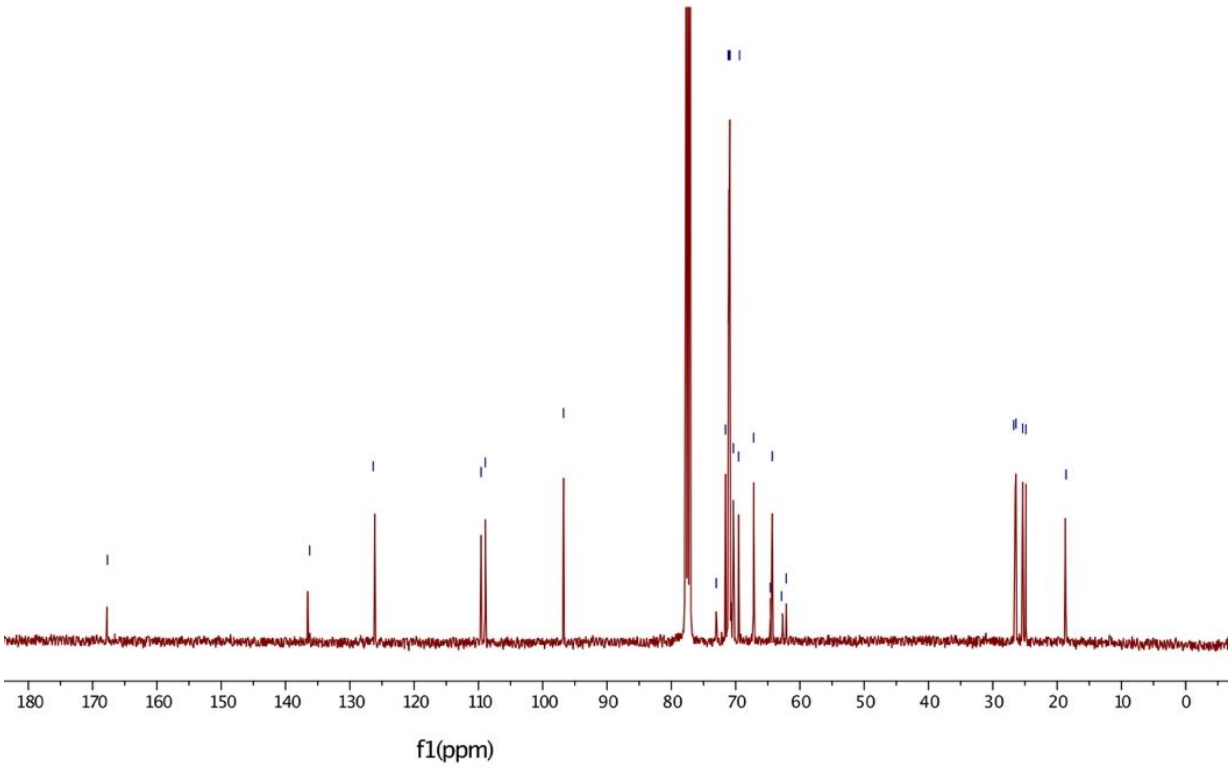

Fig. S1. ^{13}C NMR spectrum of a representative glycomonomer MEO_9IpGal in $CDCl_3$.

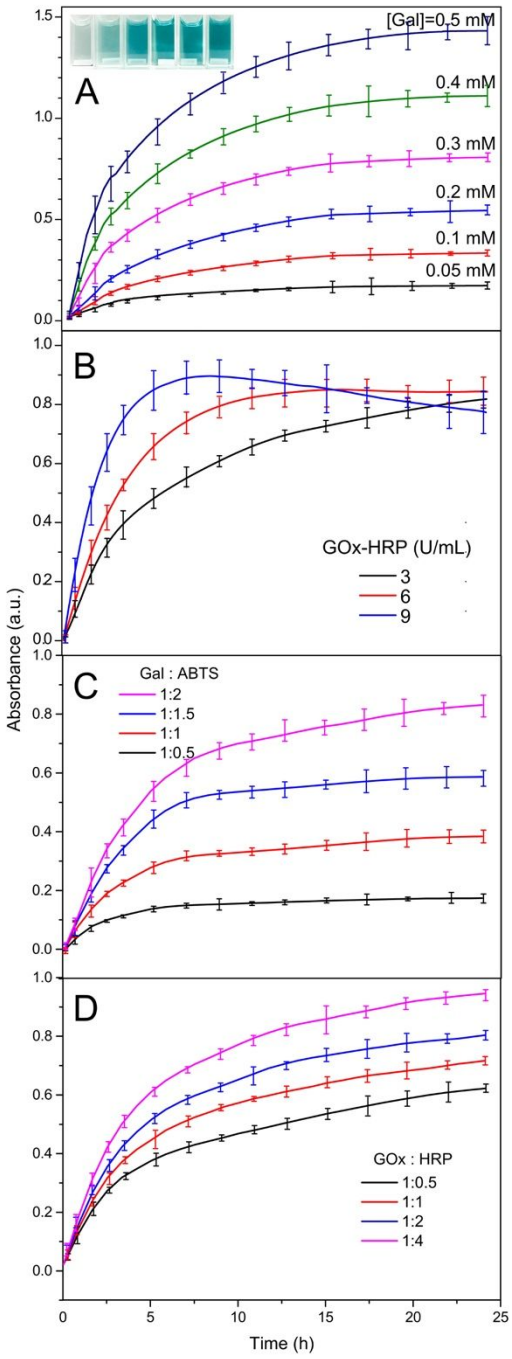

Fig. S2. UV-vis absorption at 414 nm of PBS buffer at 35 ^{o}C solutions containing (A) Gal and constant GOx (4 unit/mL). The insets show photos of the Gal samples with increasing Gal concentration from 0.05 to 0.5 mM at 24 h, (B) constant Gal (0.3 mM) and GOx of various concentrations. (C) different ratios of Gal to ABTS and (D) GOx to HRP. Adding more enzyme

shortens the time to reach a plateau but may cause inhibition due to the rapid accumulation of galactonolactone.

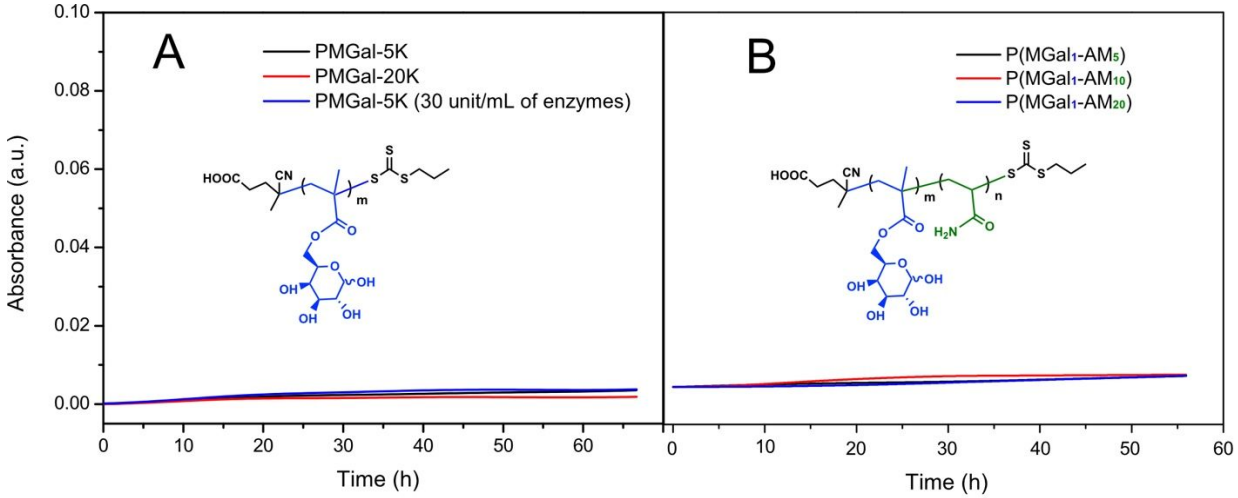

Fig. S3. UV-vis absorption curves λ = 414 nm at 35 °C of (A) PMGal and (B) P(MGal-*co*-AM) copolymer solutions (including 0.3 mM of Gal residues on the polymers) as a function of enzymatic reaction time containing ABTS (0.6 mM) and GOx (6 unit/mL).

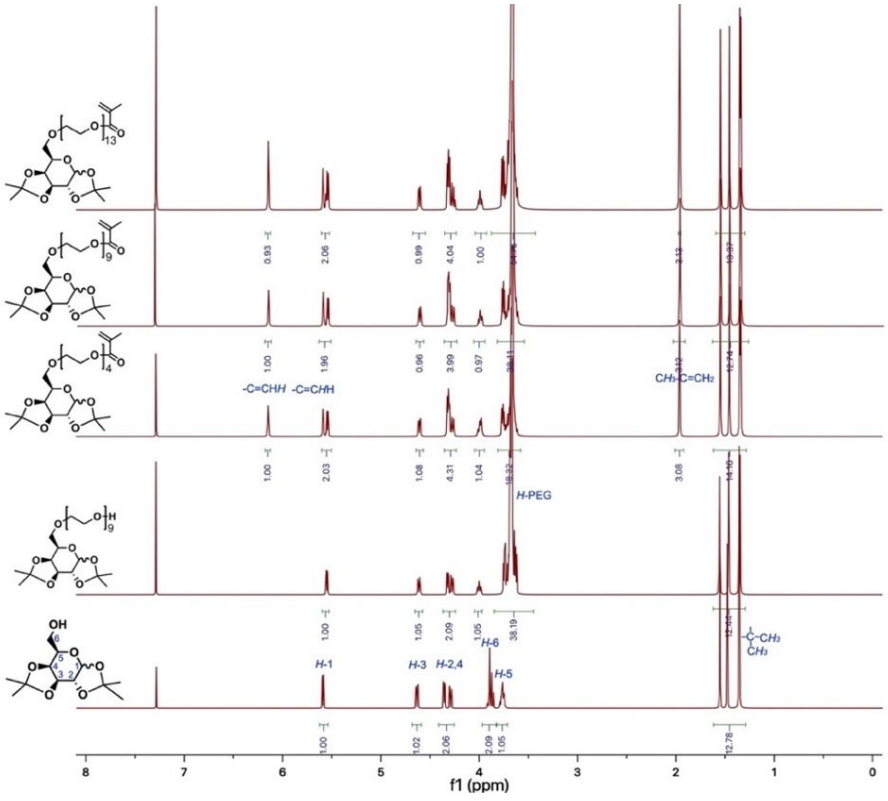

Fig. S4. ^{1}H NMR spectra of the representative intermediate products and the glycomonomers in $CDCl_3$, showing the successful PEGylation and conjugation of the methacrylate.

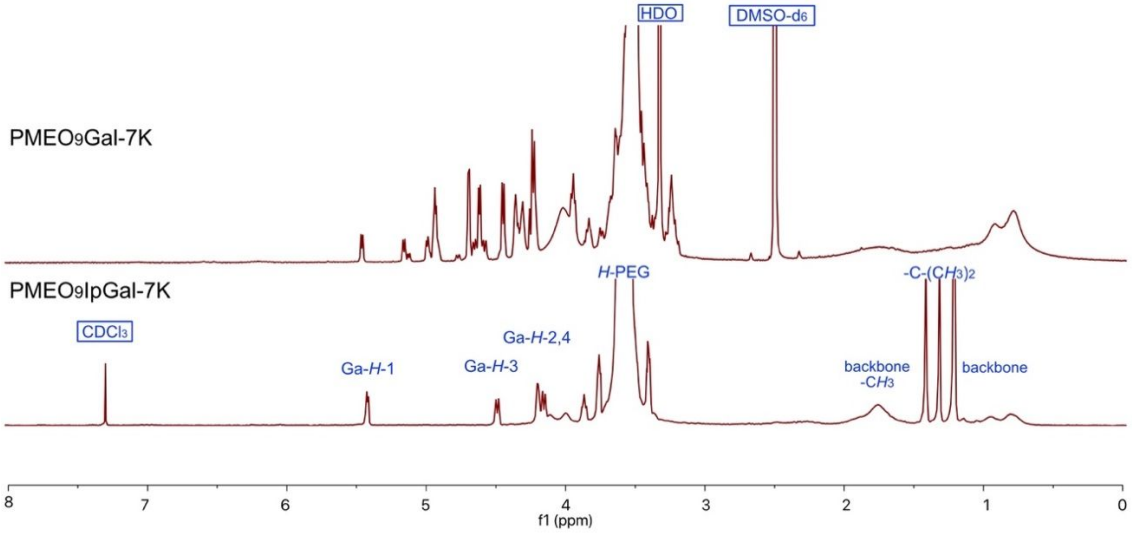

Fig. S5. ^{1}H NMR spectra of the representative glycomonomers with isopropylidene (Ip) protecting groups in $CDCl_3$ (bottom) and without Ip in DMSO-d_6 (top). The proton NMR signals of the Ip protecting groups are visible at 1.2-1.6 ppm. After deprotection, galactose shows mutarotation as α and β anomeric forms that can interconvert. The signals at 5.43 and 4.55 ppm are assigned to the protons attached to the anomeric carbon of the sugar ring. The signals at 0.7-1.2 and 1.5-2.1 ppm are assigned to the protons of methylene and methyl groups in the polymer backbone.

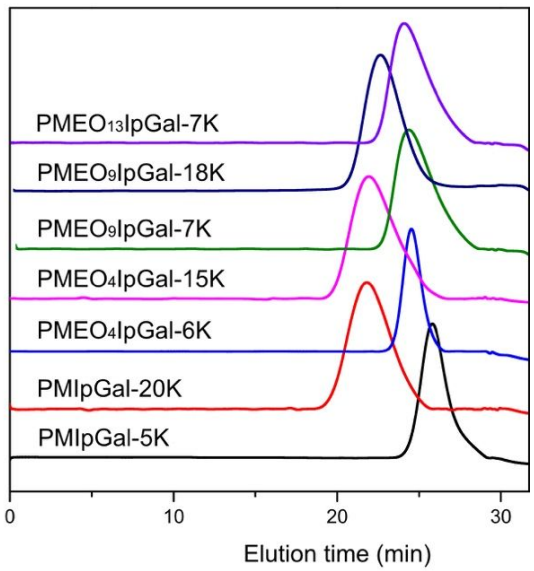

Fig. S6. SEC elution traces of the glycopolymers, all with the isopropylidene (Ip) protecting groups to keep them soluble in THF.

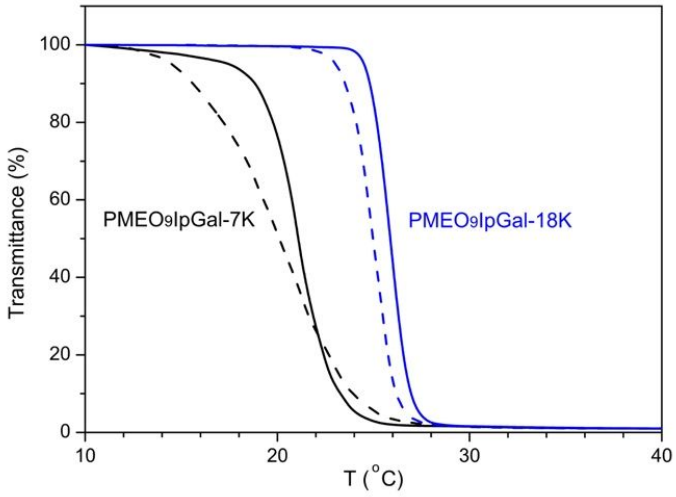

Fig. S7. Transmittance variation of aqueous solutions of selected glycopolymers (1.0 g/L) with Ip protected sugar pendant residues showing the thermoresponsiveness of the polymers during heating (solid lines) and cooling (dashes), measured at $\lambda = 400$ nm and heating or cooling rate of 0.5 °C/min.

Table S1. Characteristics of the copolymers P(MIpGal-*co*-AM) bearing galactose and acrylamide(AM)

[MIpGal]:[AM][a]		M_n (Da)[b]	Đ[b]
in feed	in copolymers		
1:5	1:5.1	7,900	1.16
1:10	1:10.8	9,100	1.14
1:20	1:21.3	8,700	1.18

[a] Determined by ^{1}H NMR. [b] Determined by SEC.