

SUPPORTING INFORMATION

The effect of linker length on ConA and DC-SIGN binding of S-glucosyl functionalized poly(2-oxazoline)s

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1. Experimental Section

1.1. Materials

4-pentenoyl chloride (98%), 10-undecenoyl chloride (97%), acetonitrile (anhydrous, 99.8%, ACN), (2-chloroethyl)trimethylammonium chloride (98%), sodium methoxide (95%, powder), 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranose (Ac₄Glc-SH, 97%), 2-ethyl-2-oxazoline (EtOx, \geq 99%), 2-Isopropenyl-2-oxazoline (iPOx, 98%) and methyl *p*-toluenesulfonate (MeOTs, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 98%), Merrifield's peptide resin (1% cross-linked), butylamine (99.5%) were purchased from Sigma Aldrich Chemical Company (Dorset, UK). EtOx, iPOx and methyl *p*-toluenesulfonate were distilled and stored over activated 4Å molecular sieves under an argon atmosphere. All other reagents and solvents were obtained at the highest purity available from Sigma Aldrich Chemical Company (Dorset, UK) and used as received unless stated otherwise. Dialysis tube (1kDa MWCO) was purchased from Spectrum Laboratories (California, USA).

1.2. Instruments and Analysis

The Emrys Liberator single-mode microwave synthesizer from Biotage equipped with a non-invasive IR sensor (accuracy: \pm 2%) was used for the microwave assisted cationic ring-opening polymerization. All polymerizations were performed with temperature control. Microwave vials were firstly heated to 120 °C and then allowed to cool to room temperature under an argon atmosphere before usage.

Proton and carbon-13 (¹H-NMR and ¹³C-NMR) nuclear magnetic resonance spectroscopy (Bruker DPX-400/600) were used to determine the chemical structure of the synthesized polymers. Samples were dissolved at 5 mg/mL concentration in CDCl₃ or MeOH-d₄ solvents depending on the solubility of the samples.

Size-exclusion chromatography (SEC) measurements were conducted on an Agilent 1260 infinity system operating in DMF with 5.0 mM NH₄BF₄ and equipped with refractive index detector (RID) and variable wavelength detector (VWD), 2 PLgel 5 μ m mixed-C columns (300 \times 7.5mm), a PLgel 5 mm guard column (50 \times 7.5mm) and an autosampler. The instrument

was calibrated with linear narrow poly(styrene) standards in range of 575 to 281,700 g.mol⁻¹. All samples were passed through 0.2 µm PTFE filter before analysis.

Gas Chromatography (GC) was used to measure monomer conversion for polymerizations. GC analysis was performed using an Agilent Technologies 7820A. An Agilent J&W HP-5 capillary column of 30 m x 0.320 mm with a film thickness of 0.25 µm was used. The oven temperature was programmed as follows: 40 °C (hold for 1 min) increase at 30 °C/min to 300 °C (hold for 2.5 min). The injector was operated at 250 °C and the FID was operated at 320 °C. Nitrogen was used as carrier gas at flow rate of 6.5 mL/min and a split ratio of 1:1 was applied. Chromatographic data was processed using OpenLab CDS ChemStation Edition, version C.01.05.

Beckman DU Series 700 UV/Vis Scanning Spectrophotometer was used to analyze the binding ability of the nanoparticles. SPR Sensorgrams were recorded in a Biorad ProteOn XPR36 SPR biosensor (Biorad, Hercules CA). Soluble DC-SIGN was immobilized to 6000 response units (RU) on discrete channels within Biorad GMC sensor chips *via* amine coupling. Soluble-phase analytes were prepared in 25 mM HEPES pH 7.4, 150 mM NaCl, 5 mM CaCl₂, 0.01% Tween-20 and flowed over the immobilized materials at a rate of 25 µL/min at 25 °C. Regeneration of the sensor chip surfaces was performed using 10 mM glycine pH 2.5.

The FT-IR spectra were recorded on a Bruker FT-IR spectrometer TENSOR II with Diamond-ATR module. The scanning range was 600-4000 cm⁻¹ and the resolution was 1 cm⁻¹.

LCST and turbidimetry measurements were performed on a Cary 100 UV-Vis spectrophotometer (Agilent) at a wavelength of 500 nm. Solutions of polymers were prepared in water (HPLC grade) at a concentration of 5 mg/mL and stirred until fully dissolved. The samples were thermostatted at 20 °C for 15 minutes prior to measurement. The transmittance was measured between 20 °C and 80 °C at a rate of 1 °C min⁻¹ in a heating and cooling cycle. The cloud points reported were determined as the 50% transmittance point during the heating cycle.

Electrospray ionization-mass spectrometry (ESI-MS) spectra were recorded on a Thermo Finnigan LCQ Decaquadropole ion trap mass spectrometer (Thermo Finnigan, San Jose,

CA), equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode and was used in positive ion mode.

1.3. Synthesis of the solid butylamine resin

Based on a literature procedure, in a 250 mL round-bottom containing a magnetic stir bar butylamine (15 g, 200 mmol) was dissolved in DMF (50 mL).¹ Merrifield's peptide resin (10 g, 40 mmol) was added into the reaction flask and refluxed overnight. The solid resin was filtered and then washed with 150 mL of dichloromethane two times until unreacted butylamine was removed. Subsequently, the obtained butylamine solid resin was dried under vacuum at ambient temperature overnight and analyzed by FT-IR.

1.4. Synthesis of 2-[2-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosylthio) propyl]-2-oxazoline ($\text{Ac}_4\text{Glc-S-Ox}$) glycomonomer

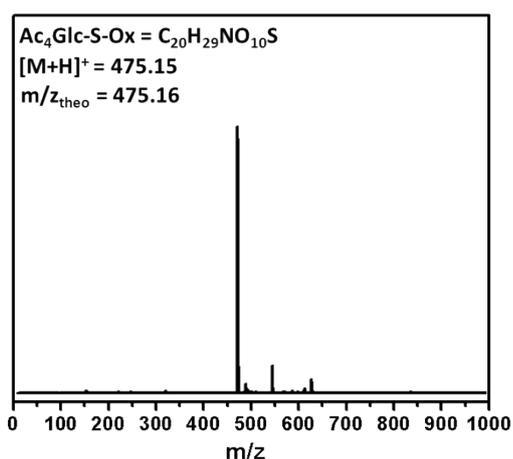
This new glycomonomer, $\text{Ac}_4\text{Glc-S-Ox}$, was synthesized by using photo-induced thiol-ene coupling reaction of the ene bond of iPOx *with* $\text{Ac}_4\text{Glc-SH}$. This easy and one-pot strategy used to synthesize *S*-glycosyl substituted 2-oxazoline is depicted in Scheme 1. The thiol-ene "click" reaction was carried out in anhydrous acetonitrile (ACN) at 365 nm UV lamp under an argon atmosphere. $\text{Ac}_4\text{Glc-SH}$ (437.3 mg, 1.2 mmol) and iPOx (133.4 mg, 1.2 mmol) were dissolved in 1.2 mL anhydrous acetonitrile and then the solid butylamine resin (203.7 mg, 0.64 mmol) as a catalyst was added into the reaction solution under an argon. After degassing the solution for 15 min, the reaction solution was irradiated at 365 nm UV lamp overnight. The reaction was followed by $^1\text{H-NMR}$ and GC. The solid butyl amine resin was filtered and the proposal chemical structure of the product was confirmed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and ESI-MS after removing of the solvent by a rotary evaporator. The product was obtained as a pale white gummy material. (553.5 mg, yield: 97%) The obtained product was used directly for copolymerization without any further purification.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K, ppm): δ = 5.24 (1H, m, H-3), 5.00-5.11 (1H, m, H-4), 4.57-5.01 (1H, m, H-2), 4.51 (1H, dd, J = 9.9 Hz, H-1), 4.24 (2H, t, J = 9.6 Hz, $\text{NCH}_2\text{CH}_2\text{O}$), 4.08-4.19 (2H, m, H-6), 3.83 (2H, t, J = 9.6 Hz, $\text{NCH}_2\text{CH}_2\text{O}$), 3.72 (1H, m, H-5), 2.92-3.08 (1H, m,

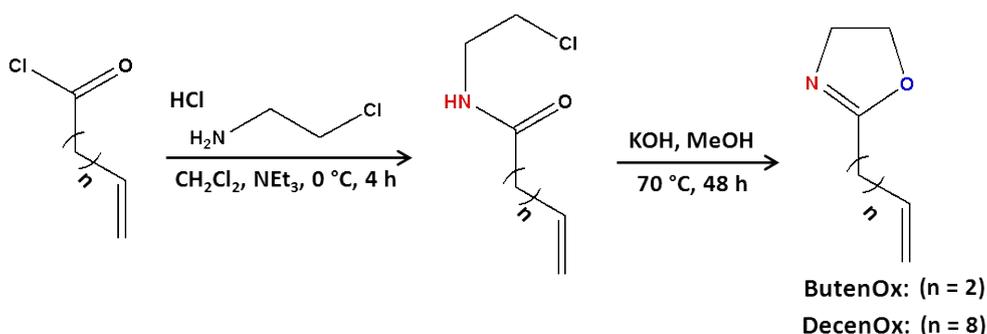
CH₂CH₃CHCN(O)), 2.63 (2H, m, CH₂CH₃CHCN(O)), 1.99, 2.04, 2.09, 2.16 (12H, 4s, COCH₃), 1.22 (3H, dd, J= 9.4 Hz, CHCH₃).

¹³C-NMR (400 MHz, CDCl₃, 298 K, ppm): δ = 173.45-174.17, 161.26, 84.78, 76.81, 74.36, 69.49, 68.71, 67.54, 53.67, 32.83, 31.23, 19.89, 17.47.

ESI-MS m/z: calculated for C₂₀H₂₉NO₁₀S (M+H⁺), 475.15; found, 475.16.



1.5. Synthesis of 2-butenyl-2-oxazoline (ButenOx)



Scheme S1. Reaction scheme for the synthesis of 2-butenyl-2-oxazoline (ButenOx) and 2-decenyl-2-oxazoline (DecenOx).

ButenOx and DecenOx were prepared according to the procedure reported by Kempe *et al.*² 4-pentenoyl chloride (5.37 g, 0.045 mol) and 2-chloroethylammonium chloride (5.33 g, 0.046 mol) were suspended in 100 mL anhydrous dichloromethane and then the reaction solution was cooled to 0 °C. Subsequently, triethylamine (Et₃N) (14.6 mL, 0.104 mol) were added

dropwise within one hour and the reaction mixture was stirred for three more hours at room temperature. The reaction was terminated by adding 30 mL water. The aqueous phase was extracted 3 times with 25 mL dichloromethane and then the combined organic phases were washed with water and brine, respectively. After drying over magnesium sulfate (MgSO₄), the solvent was removed by a rotary evaporator and then the obtained crude product was dissolved in methanol and used for next step without any further purification. A 25 wt% solution of potassium hydroxide (KOH) in methanol (MeOH) was added dropwise into the solution and the reaction solution was heated to 70 °C and stirred for 48 h. After removing of MeOH under reduced pressure, 30 mL of water was added and extracted 3 times with diethyl ether and then the combined organic phases were washed with water and brine again. After drying over magnesium sulfate (MgSO₄), the solvent was removed by a rotary evaporator and then the obtained crude product was purified by distillation (55 °C, 1.2 × 10⁻² mbar) to give 2.26 g (0.018 mol) of ButenOx in 42% yield (relative to the 4-pentenoyl chloride).

¹H-NMR (400 MHz, CDCl₃, 298 K, ppm): δ = 5.76-5.88 (m, 1H, CHCH₂), 4.96-5.10 (m, 2H, CHCH₂), 4.21 (t, 2H, *J* = 9.0 Hz, OCH₂), 3.82 (t, 2H, *J* = 9.0 Hz, NCH₂), 2.34-2.42 (m, 4H, CH₂).

¹³C-NMR (400 MHz, CDCl₃, 298 K, ppm): δ = 167.76, 138.97, 118.61, 67.35, 54.52, 29.37, 27.44.

ESI-MS *m/z*: calculated for C₇H₁₁NO (M+H⁺), 125.08; found, 125.10.

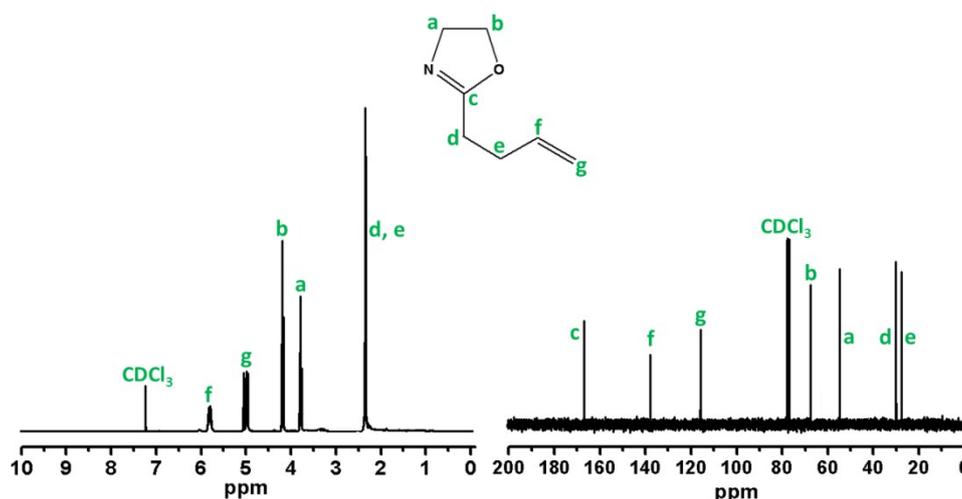


Figure S.1. Details of ¹H-NMR and ¹³C-NMR spectrum of ButenOx.

1.6. Synthesis of 2-decenyl-2-oxazoline (DecenOx)

10-undecenoylchloride (10 g, 0.084 mol) and 2-chloroethylammonium chloride (9.86 g, 0.085 mol) were suspended in 200 mL anhydrous dichloromethane and then the reaction solution was cooled to 0 °C. Subsequently, Et₃N (27 mL, 0.193 mol) were added dropwise within one hour and the reaction mixture was stirred for three more hours at room temperature. The reaction was terminated by adding 60 mL water. The aqueous phase was extracted 3 times with 50 mL dichloromethane and then the combined organic phases were washed with water and brine, respectively. After drying over MgSO₄, the solvent was removed by a rotary evaporator and then the obtained crude product was dissolved in methanol and used for next step without any further purification. A 25 wt% solution of KOH in MeOH was added dropwise into the solution and the reaction solution was heated to 70 °C and stirred for 48 h. After removing of MeOH under reduced pressure, 60 mL of water was added and extracted 3 times with diethyl ether and then the combined organic phases were washed with water and brine again. After drying over MgSO₄, the solvent was removed by a rotary evaporator and then the obtained crude product was purified by distillation (85 °C, 1.2 × 10⁻² mbar) to give 7.2 g (0.034 mol) of DecenOx in 72% yield (relative to the 10-undecenoylchloride).

¹H-NMR (400 MHz, CDCl₃, 298 K, ppm): δ = 5.80 (m, 1H, CH₂), 4.95 (m, 2H, CH), 4.21 (t, 2H, *J* = 9.6 Hz, CH₂), 3.81 (t, 2H, *J* = 9.6 Hz, CH₂), 2.26 (t, 2H, *J* = 7.6 Hz, CH₂), 2.03 (m, 2H, CH₂), 1.61 (m, 2H, CH₂), 1.31 (m, 10H, CH₂).

¹³C-NMR (400 MHz, CDCl₃, 298 K, ppm): δ = 169.63, 138.26, 114.91, 68.65, 54.19, 33.85, 29.83, 29.21, 29.10, 28.92, 25.87, 24.94, 23.67.

ESI-MS *m/z*: calculated for C₁₃H₂₃NO (M+H⁺), 209.18; found, 209.23.

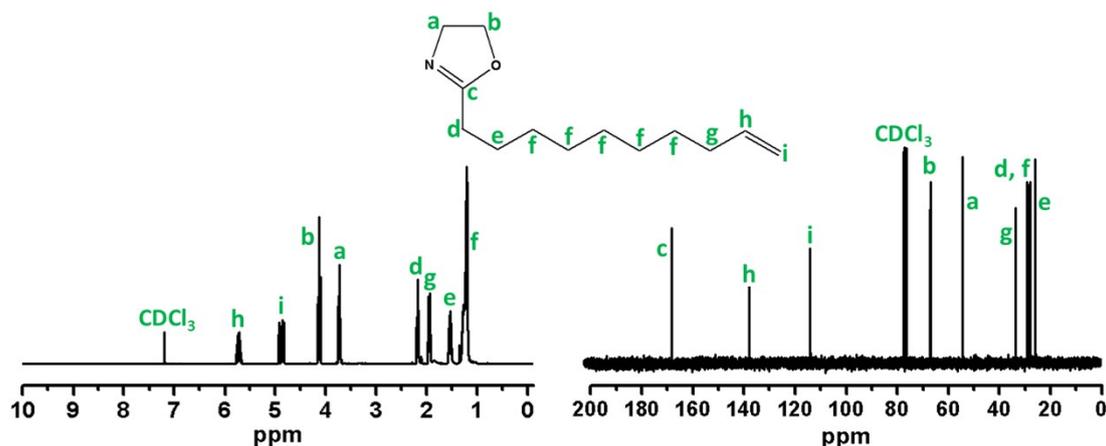


Figure S.2. Details of ^1H -NMR and ^{13}C -NMR spectrum of DecenOx.

1.7. Microwave-assisted copolymerization of EtOx with $\text{Ac}_4\text{Glc-S-Ox}$, ButenOx and DecenOx

As a general procedure, a polymerization solution of initiator (methyl *p*-toluenesulfonate), monomers (EtOx, $\text{Ac}_4\text{Glc-S-Ox}$, ButenOx and DecenOx) and solvent (acetonitrile) was prepared. The total monomer concentration was adjusted to 1 M with a [EtOx]:[targeting monomer]:[I] = 55:5:1, 50:10:1, 45:15:1 for each targeting monomer, respectively. Preheated to 150 °C microwave vials were allowed to cool to room temperature under an argon atmosphere before the polymerization solutions was transferred into vials. Vials were capped and the solutions were allowed to polymerize at 120 °C for 12 h in the microwave synthesizer. After cooling, the reaction was quenched by the addition of 25 μL MeOH. Samples were taken for GC, ^1H NMR and GPC analysis to determine the monomer conversions and the molar mass and dispersity (\mathcal{D}) of the polymers. For the calculations of the monomer conversions, the polymerization solvent was used as internal standard. The obtained copolymers were purified by precipitation in ice-cold diethyl ether for twice and then dried in a vacuum oven at 40 °C for 3 h.

Table S.1. Summary of monomer conversions, number average molar masses (M_n) and molar mass distributions (\mathcal{D}) of cationic ring opening polymerization of the statistical copolymers.

Polymer Code	[EtOx]:[Targeted Mon]:[I] ^a	ρ^b (%)		$M_{n, GPC}^c$ (g.mol ⁻¹)	\mathcal{D}
		EtOx	Targeted Mon		
P1a1 = P((EtOx) ₅₅ -co-(Ac ₄ Glc-S-Ox) ₅)	55:5:1	99	98	8400	1.19
P1b1 = P((EtOx) ₅₀ -co-(Ac ₄ Glc-S-Ox) ₁₀)	50:10:1	98	97	10900	1.21
P1c1 = P((EtOx) ₄₅ -co-(Ac ₄ Glc-S-Ox) ₁₅)	45:15:1	98	97	12800	1.23
P2a1 = P((EtOx) ₅₅ -co-(ButenOx) ₅)	55:5:1	99	99	7600	1.15
P2b1 = P((EtOx) ₅₀ -co-(ButenOx) ₁₀)	50:10:1	99	99	7400	1.16
P2c1 = P((EtOx) ₄₅ -co-(ButenOx) ₁₅)	45:15:1	98	98	7800	1.16
P3a1 = P((EtOx) ₅₅ -co-(DecenOx) ₅)	55:5:1	99	99	7900	1.15
P3b1 = P((EtOx) ₅₀ -co-(DecenOx) ₁₀)	50:10:1	98	98	8600	1.15
P3c1 = P((EtOx) ₄₅ -co-(DecenOx) ₁₅)	45:15:1	98	97	9700	1.16

^a) Initial molar ratio of monomers to initiator; ^b) Conversion (ρ) obtained from ¹H NMR and GC analysis; ^c) Determined by DMF GPC (relative to PS stn.)

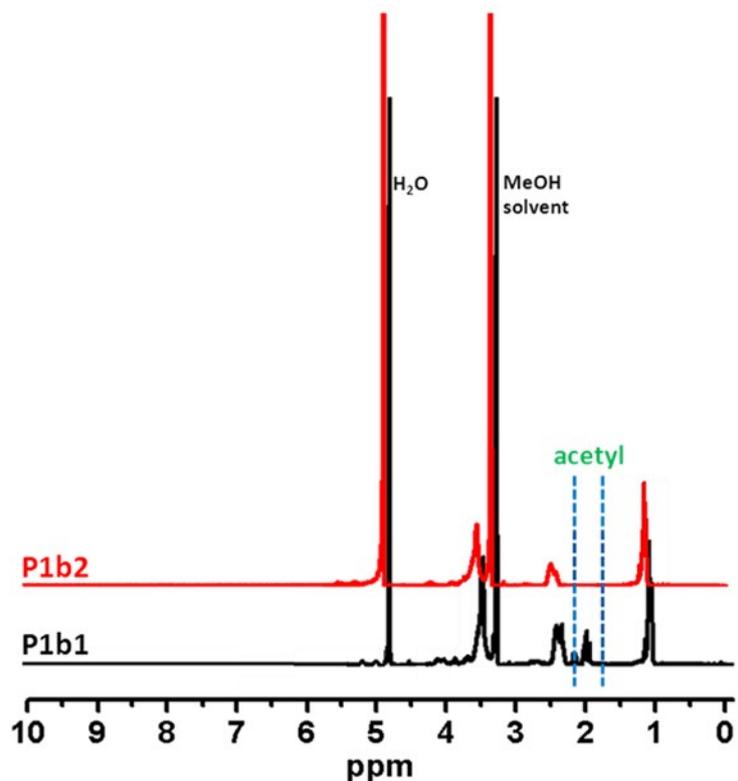


Figure S.3. ^1H NMR characterization of the synthesized glyco-copolymer (EtOx and $\text{Ac}_4\text{Glc-S-Ox}$), before (**P1b1**) and after (**P1b2**) the deprotection of the acetyl groups.

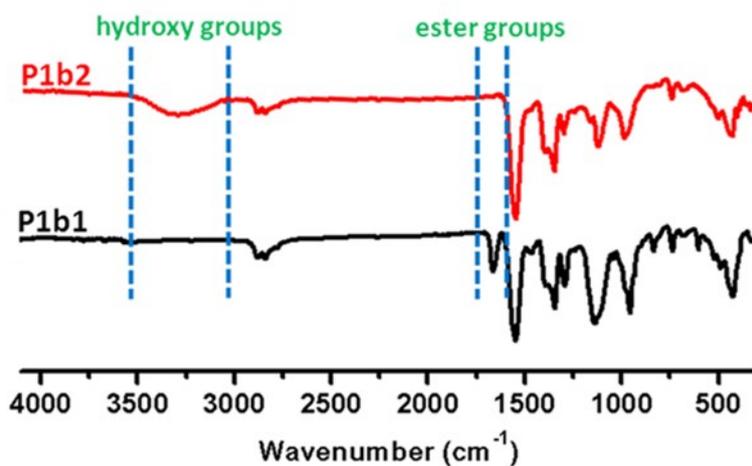
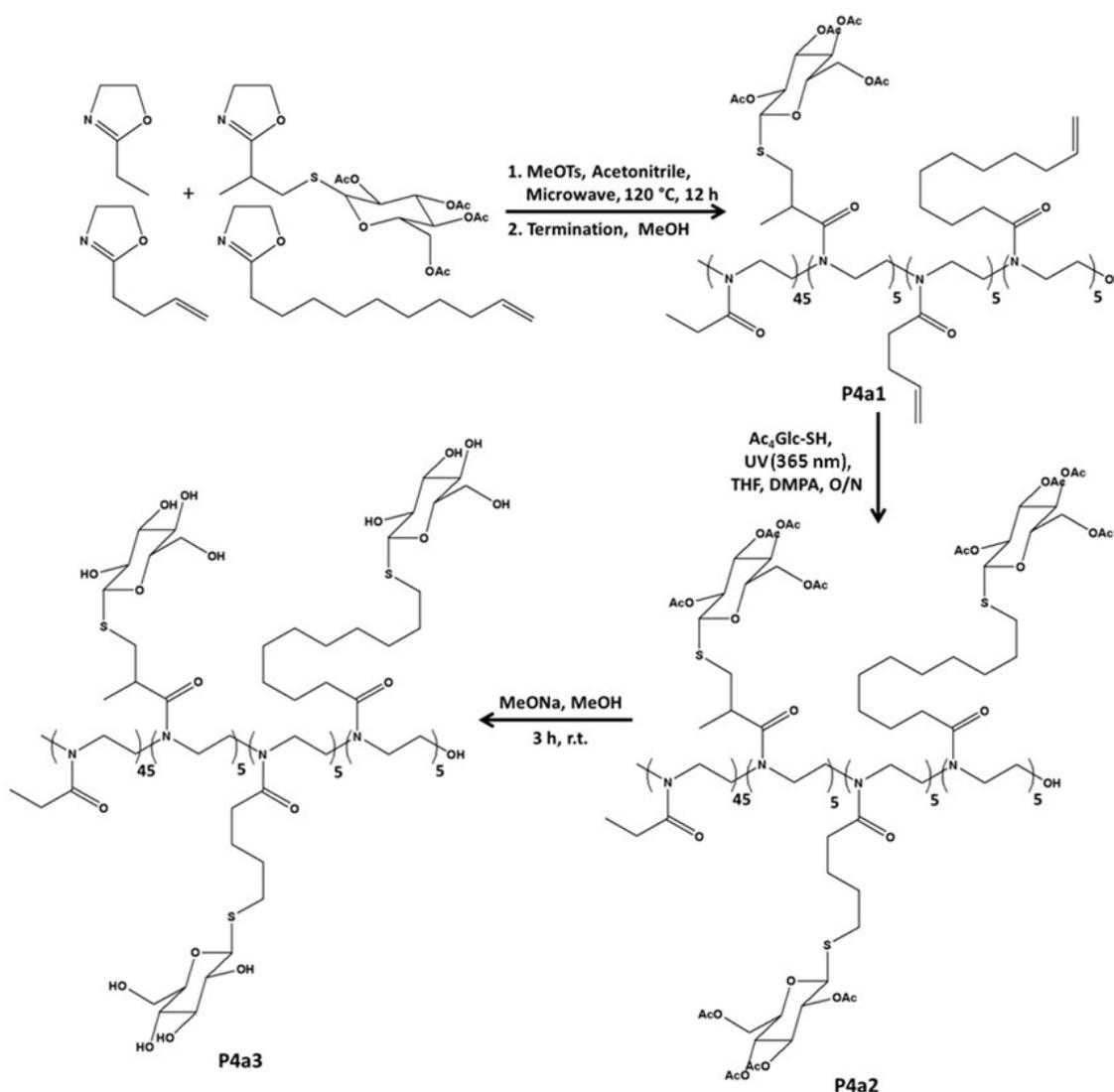


Figure S.4. FT-IR spectra of the synthesized glyco-copolymer (EtOx and $\text{Ac}_4\text{Glc-S-Ox}$), **P1b1** and **P1b2** (after deacetylation) demonstrating acetyl-protected glucose units (ester band at 1755 cm^{-1}) onto the polymer precursor. The disappearance of the ester band as well as the appearance of a broad band between 3100 cm^{-1} and 3600 cm^{-1} confirms the successful deprotection of the sugar moieties.

1.8. Preparation of the copoly(EtOx-ButenOx-DecenOx-Ac₄Glc-S-Ox) P4a1



Scheme S.2. Schematic representation of the cationic ring-opening copolymerization of EtOx, Ac₄Glc-S-Ox, ButenOx and DecenOx ([M]/[I] = 60, EtOx 45, Ac₄Glc-S-Ox 5, ButenOx 5 and DecenOx 5); Thiol-ene reaction and also the deprotection reaction of the copolymer (**P4a1**).

A solution containing initiator, monomers (EtOx, ButenOx, DecenOx and Ac₄Glc-S-Ox), and solvent (acetonitrile) was polymerized at 120 °C for 12 h in the microwave synthesizer. The total monomer concentration was 1.0 M again and a total monomer to initiator ([M]/[I]) ratio of 60 was applied containing same mole ratio (8.3%) for ButenOx, DecenOx and Ac₄Glc-S-Ox (EtOx 45, ButenOx 5, DecenOx 5 and Ac₄Glc-S-Ox 5). The conversion of monomers was followed GC and ¹H NMR. The obtained copolymer was purified by precipitation in ice-cold diethyl ether for twice and then dried in a vacuum oven at 40 °C for 3 h.

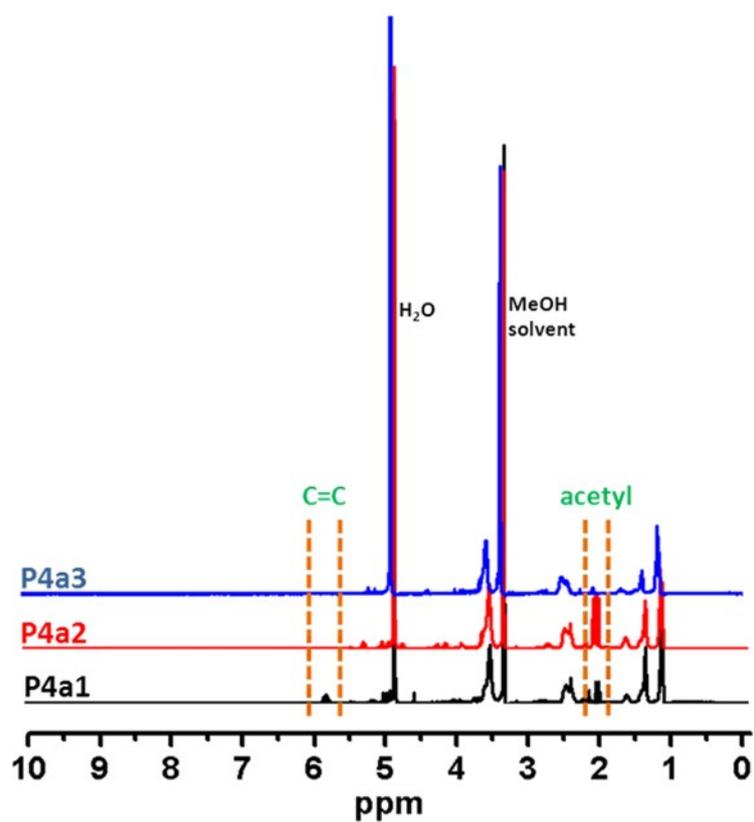


Figure S.5. ^1H NMR characterization (400 MHz, CD_3OD) of the obtained copolymers **P4a1**, **P4a2** (thiol-ene product) and **P4a3** (after deacetylation).

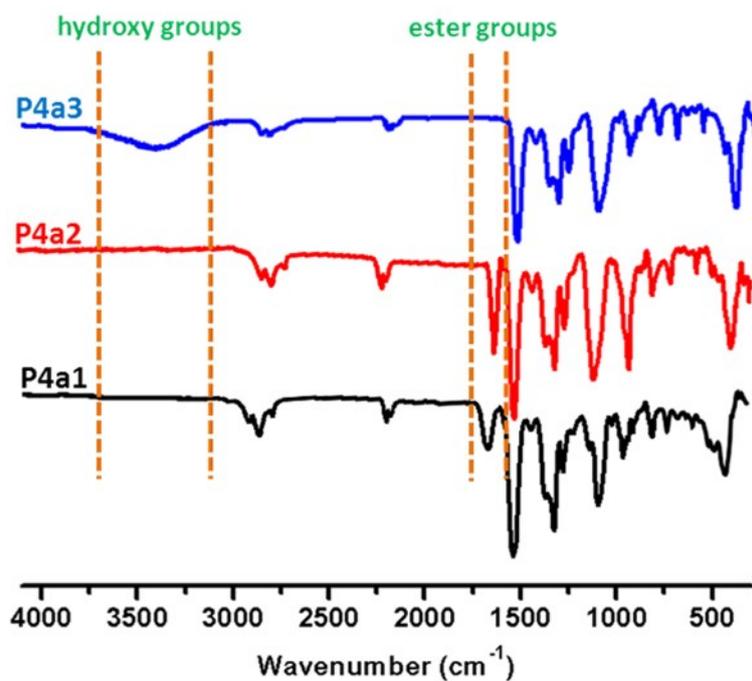


Figure S.6. FT-IR spectra of **P4a1**, **P4a2** (thiol-ene product) and **P4a3** (after deacetylation) demonstrating successful addition of acetyl-protected glucose units (ester band at 1755 cm^{-1} onto the polymer precursor. The disappearance of the ester band as well as the appearance of a broad band between 3100 cm^{-1} and 3600 cm^{-1} confirms the successful deprotection of the sugar moieties.

1.9. Thiol-ene Photoaddition Reactions of poly(EtOx-co-ButenOx)s and poly(EtOx-co-DecenOx)s using $\text{Ac}_4\text{Glc-SH}$

The synthesized copolymers (75-100 mg) were dissolved in 3 mL dry THF and $\text{Ac}_4\text{Glc-SH}$ was added in 1.2-fold excess with respect to the double bonds. After the addition of 2,2-dimethoxy-2-phenylacetophenone (DMPA), the reaction solutions were degassed for 30 min and then irradiated at 365 nm UV lamp overnight. The resulting copolymers were purified by precipitation in ice-cold diethyl ether for twice and then dried in a vacuum oven at $40\text{ }^\circ\text{C}$ for 3 h.

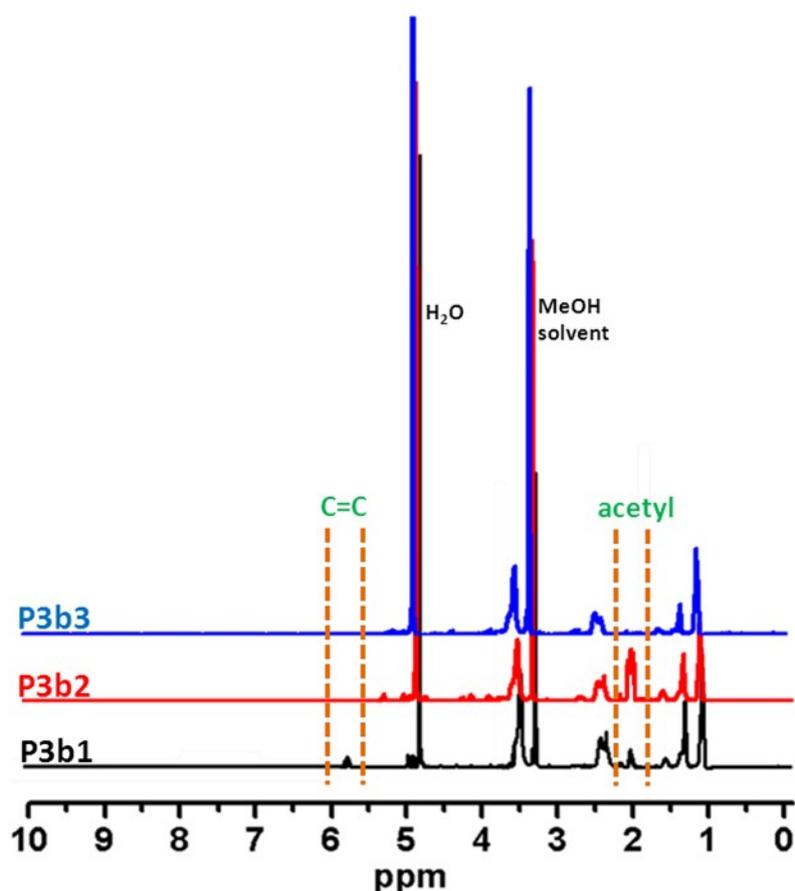


Figure S.7. ^1H NMR characterization (400 MHz, CD_3OD) of the obtained copolymers **P3b1**, **P3b2** (thiol-ene product) and **P3b3** (after deacetylation).

1.10. Deprotection of the synthesized acetyl-protected glyco-copolymers

The obtained protected glycopolymers (100-150 mg) were dissolved in 5 mL MeOH. 1 mL of 2.0 M sodium methoxide solution was added and the reaction solution was stirred for 3 h. After the removal of MeOH *via* rotary evaporator, the obtained polymer re-dissolved in water and neutralized with diluted HCl solution. Subsequently, the mixture was directly transferred to one dialysis tubing and dialyzed against water for 3 days after which the glycopolymer could be recovered by freeze drying.

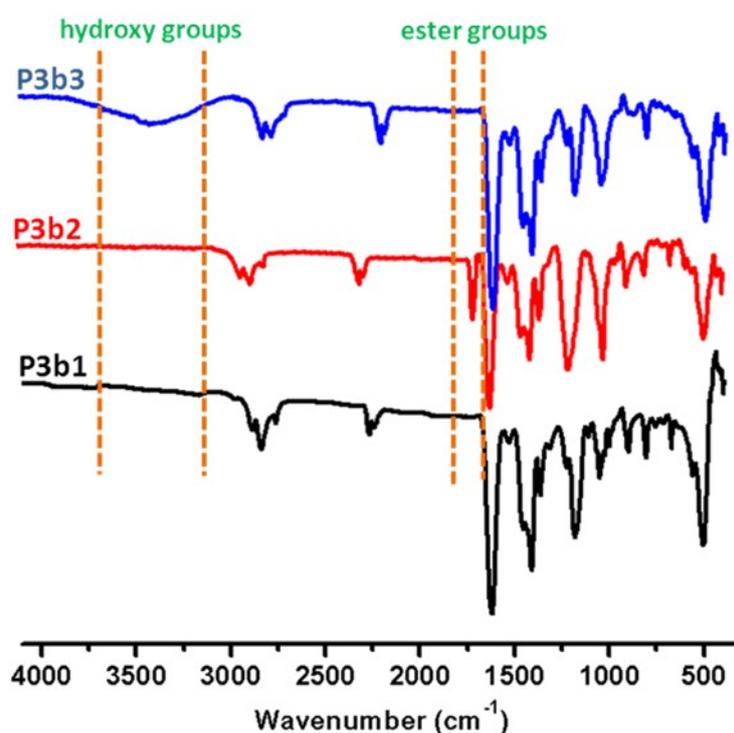
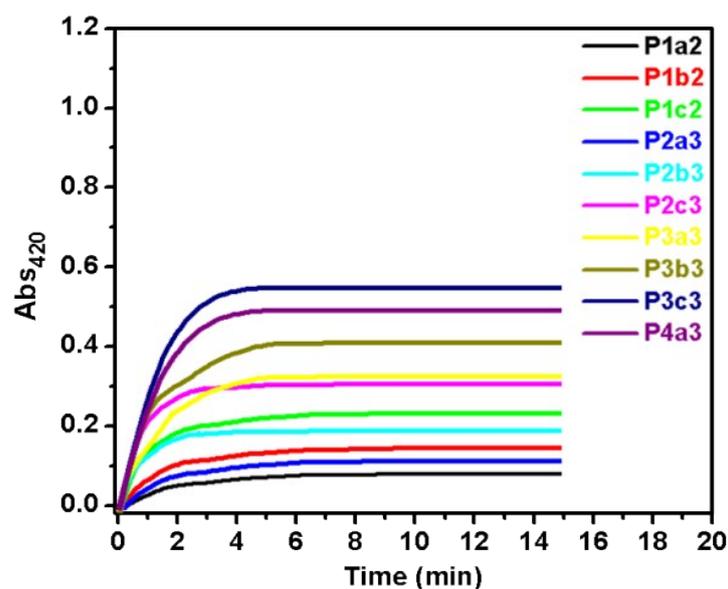


Figure S.8. FT-IR spectra of **P3b1**, **P3b2** (thiol-ene product) and **P3b3** (after deacetylation) demonstrating successful addition of acetyl-protected glucose units (ester band at 1755 cm^{-1}) onto the polymer precursor. The disappearance of the ester band as well as the appearance of a broad band between 3100 cm^{-1} and 3600 cm^{-1} confirms the successful deprotection of the sugar moieties.

1.11. Cloud point measurements

The glyco-copolymers were dissolved in HPLC grade water at a constant concentration of 5 mg/mL. The turbidity of the solutions was determined in two temperature cycles ranging from 20 to 80 °C at a rate of 1 °C min⁻¹ in a heating and cooling cycle. The cloud point temperatures were determined at 50% transmittance.



1.12. Lectin binding studies

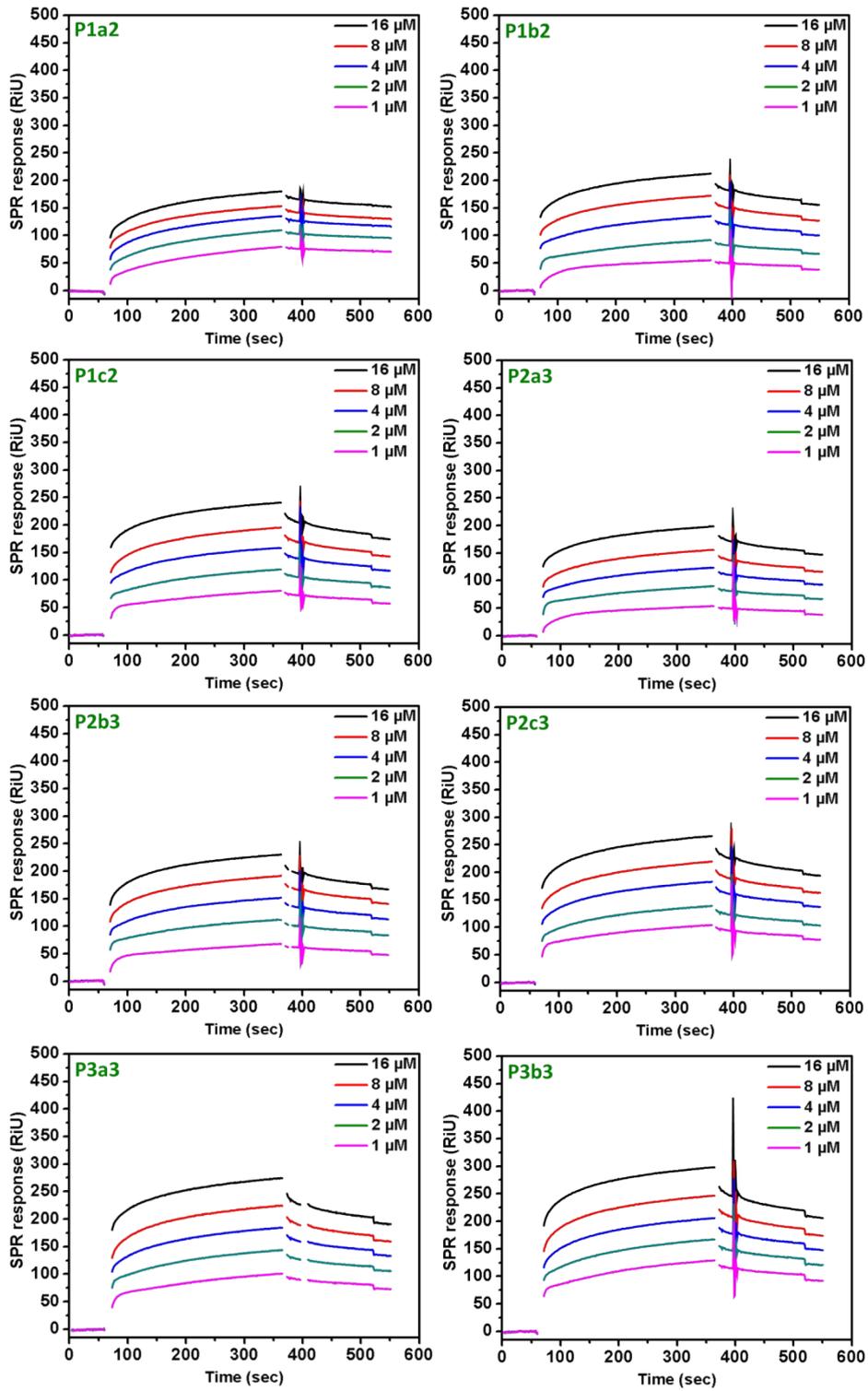
1.12.1. Turbidimetry assay

All experiments were conducted with HEPES-buffered saline (HBS) (0.10 M HEPES, 0.9 M NaCl, 1 mM MgCl₂, 1 mM CaCl₂, and 1 mM MnCl₂ adjusted to pH 7.4 and filtered with 0.2 μm regenerated cellulose syringe filter. A solution of 120 μM ConA in HBS buffer solution was prepared fresh before the assay. Turbidity measurements were performed by adding 350 μL of the ConA solution to a dry quartz microcuvette and put into the holder of UV-visible spectrophotometry at a certain temperature for 1 min. A solution of the ligand in HBS buffer (350 μL at 640 μM) was added into into the cuvette *via* a pipette, the absorbance of the mixture was quickly recorded at 420 nm for 15 min every 0.12 s.

Figure S9. Turbidity measurements of the obtained glycopolymers with ConA.

1.12.2. Surface Plasmon Resonance

Surface Plasmon Resonance (SPR) was used for interaction analysis through DC-SIGN. The extent of interaction between the glycopolymers and lectins were performed on a BIAcore 2000 system (GE Healthcare). DC-SIGN (0.005 mg/ml) were immobilized *via* a standard amino coupling protocol onto a CM5 sensor chip that was activated by flowing a 1:1 mixture of 0.1 M *N*-hydroxysuccinimide and 0.1 M *N*-ethyl-*N'*-(dimethylaminopropyl)carbodiimide over the chip for 5 min at 25 °C at a flow rate of 5 μ L/min after the system equilibration with HEPES filtered buffer (10 mM HEPES pH 7.4, 150 mM NaCl, 5 mM CaCl₂). Subsequently, channels 1 (blank), 2, 3 and 4 were blocked by following a solution of ethanolamine (1 M pH 8.5) for 10 min at 5 μ L/min to remove remaining reactive groups on the channels. Sample solutions were prepared at varying concentrations (16 μ M-1 μ M) in the same HEPES buffer to calculate the binding kinetics. Sensorgrams for each glycopolymer concentration were recorded with a 300 seconds injection of polymer solution (on period) followed by 150 seconds of buffer alone (off period). Regeneration of the sensor chip surfaces was performed using 10 mM HEPES pH 7.4, 150 mM NaCl, 10 mM EDTA, 0.01% P20 surfactant solution. Kinetic data was evaluated using a single set of sites (1:1 Langmuir Binding) model *via* the BIAevaluation 3.1 software.



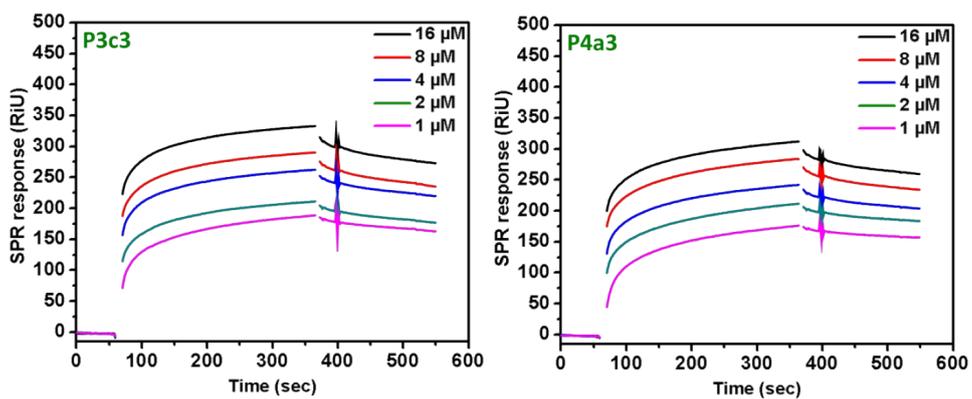


Figure S10. SPR sensorgrams showing concentration-dependent interactions between glycopolymers synthesized and DC-SIGN.

2. References

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- 2 Kempe, K.; Vollrath, A.; Schaefer, H. W.; Poehlmann, T. G.; Biskup, C.; Hoogenboom, R.; Hornig, S.; Schubert, U. S. *Macromolecular Rapid Communications*, 2010, **31**, 1869.