Supporting Information

Templating Carbohydrate-functionalised Polymer-Scaffolded Dynamic Combinatorial Libraries with Lectins

Clare S. Mahon,^{a,b} Martin A. Fascione,^{b,c} Chadamas Sakonsinsiri,^b Tom E. McAllister,^b W. Bruce Turnbull,^b and David A. Fulton^a*

^aChemical Nanoscience Laboratory, School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

^bSchool of Chemistry and Astbury Centre for Structural Molecular Biology, University of Leeds, Leeds, LS2 9JT, UK

^cDepartment of Chemistry, University of York, Heslington, York, YO10 5DD, UK

email: david.fulton@ncl.ac.uk

All solvents were dried prior to use according to standard methods.¹ *N*, *N*-dimethylacrylamide was purified by vacuum distillation at 60 °C, boron trifluoride diethyletherate (BF₃.OEt₂) was distilled over CaH₂, and all other commercially available reagents were used as received. Where appropriate anhydrous quality material was purchased. All solvents used for flash chromatography were GPR grade, except hexane and ethyl acetate, when HPLC grade was used. All synthetic procedures to afford acylhydrazides **GAL** and **MAN** were performed in oven-dried glassware under a $N_{2(g)}$ atmosphere.

¹H and ¹³C NMR spectra of aldehyde monomer M1 and associated precursors were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz respectively, or on a JEOL ECS-400 spectrometer at 400 MHz and 100 MHz, with the residual solvent signal as an internal standard. Highresolution mass spectrometry of aldehyde monomer M1 and associated precursors was performed on a Waters LCT premier mass spectrometer (Waters Inc.). ¹H NMR spectra of GAL and MAN, and associated precursors, were recorded on a Bruker Avance 500 spectrometer at 500 MHz, or on an Bruker Avance 300 spectrometer at 300 MHz. The following abbreviations are used in ¹H NMR analysis: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, dt = doubletdouble triplet, td = triple doublet, ddd = double double doublet. ¹H-NMR data of monosaccharides are assigned in agreement with Fig. 1. ¹³C NMR spectra of GAL and MAN, and associated precursors, were recorded on a Bruker Avance 500 spectrometer at 500 MHz. Electrospray (ES+) ionisation mass spectra of GAL and MAN and associated precursors were obtained on a Micromass LCT-KA111 mass spectrometer, with high resolution ES+ spectra obtained on a Bruker Daltonics MicroTOF mass spectrometer. Isotopic ratios were calculated by comparison of the ¹³C peak area of the most abundant ion, using Bruker Compass Data Analysis 4.0 software. Infra-red spectra of GAL and MAN and associated precursors were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Optical rotations were measured at the sodium D-line with an Optical Activity AA-1000 polarimeter. $[\alpha]_D$ values, where quoted, are givin in units of 10⁻¹ deg cm² g⁻¹. Analytical TLC was performed on silica gel 60-F²⁵⁴ (Merck) with detection by fluorescence and/or charring following immersion in 5% H₂SO₄/methanol solution. Gel permeation chromatography (GPC) was conducted on a Varian ProStar instrument (Varian Inc.) equipped with a Varian 325 UV-Vis dual wavelength detector (254 nm), a Dawn Heleos II multi-angle laser light scattering detector (Wyatt Technology Corp.), a Viscotek 3580 differential RI detector, and a pair of PL gel 5 μ m Mixed D 300 \times 7.5 mm columns with guard column (Polymer Laboratories Inc.) in series. Near monodisperse methyl methacrylate standards

(Agilent Technologies) were used for calibration. Data collection was performed with Galaxie software (Varian Inc.) and chromatograms analyzed with the Cirrus software (Varian Inc.) and Astra software (Wyatt Technology Corp.). Fluorescence spectroscopy was carried out on a Fluoromax instrument, with corrected spectra used for all analysis.

¹H NMR spectra of PS-DCLs were measured using a JEOL Lambda spectrometer (¹H at 500 MHz) and analysed using MestreNova. PS-DCLs were prepared so as to contain 25.0 mM concentrations of acylhydrazides **GAL** and **MAN**, with **P1** present at a concentration of 1.85 mM. Equilibration to a 1.0:1.0 ratio of **GAL** to **MAN** in solution was confirmed by ¹H NMR spectroscopic analysis prior to addition of templates. Con A and LTB were added to PS-DCLs at concentrations of 5.0 mg mL⁻¹.



Fig. 1 Proton numbering in ¹H-NMR data for gluco-configured monosaccharides.

Experimental Procedures:



Scheme 1 Synthesis of *N*-ethylacrylamide-2-(4-formylbenzamide) (M1): (i) CH(OCH₃)₃, MeOH, H₂SO₄, 80 °C, 48 h. (ii) 1,2-diaminoethane, 130 °C, 24 h. (iii) Acryloyl chloride, Et₃N, CH₂Cl₂, 0 °C, 16 h. (iv) 1M HCl_(aq), 2 h.

Methyl 4-(dimethoxymethyl)benzoate² (1):

A solution of 4-carboxybenzaldehyde (15.4 g, 102.6 mmol), trimethylorthoformate (32.7 g, 307.8 mmol) and H₂SO₄ (8 drops) in MeOH (100 mL) was heated under reflux for 48 h. The reaction mixture was transferred to a separating funnel with saturated NaHCO_{3(aq)} (100 mL). The aqueous layer was extracted with CH₂Cl₂ (3×150 mL). The organic extracts were combined and dried over Na₂SO₄, filtered and evaporated to dryness to afford a crude liquid which was purified by vacuum distillation to afford the title product as a clear liquid (19.8 g, 92%). ¹H NMR (300 MHz, CDCl₃): δ 3.30 (s, 6H, CH(OCH₃)₂), 3.89 (s, 3H, OCH₃), 5.42 (s, 1H, CH(OCH₃)₂), 7.51 (d, 2H, Ar, J = 8.1 Hz), 8.02 (d, 2H, Ar, J = 8.1 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 52.2, 53.0, 103.0, 127.1, 129.8, 130.8, 143.8, 167.1.

N-Ethylacrylamide-2-(4-(dimethoxymethyl)benzamide)³ (2):

A solution of methyl 4-(dimethoxymethyl)benzoate **1** (6.0 g, 28.5 mmol) in 1,2-diaminoethane (100 mL) was heated under reflux for 24 h then evaporated to dryness. The viscous yellow oil obtained was dissolved in CH_2Cl_2 (100 mL) and Et_3N (5.7 g, 56.3 mmol) added. The solution was cooled to 0 °C in an ice bath. Acryloyl chloride (2.6 g, 28.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise over 30

min. The reaction was stirred overnight at room temperature then transferred to a separating funnel with saturated NaHCO_{3(aq)} (150 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 150 mL). The organic extracts were combined and dried over Na₂SO₄, filtered and evaporated to dryness to afford a crude solid which was purified by column chromatography [SiO₂, EtOAc-Et₃N (95:5)] to afford the title product as a white solid (3.3 g, 40 %). ¹H NMR (300 MHz, CDCl₃): δ 3.28 (s, 6H, CH(OCH₃)₂), 3.52 (m, 4H, (CH₂)₂), 5.37 (s, 1H, CH(OCH₃)₂), 5.58 (dd, 1H, J = 9.6 Hz), 6.14 (dd, 1H, J = 17.1 Hz), 6.23 (dd, 1H, J = 17.1 Hz), 7.37 (s, 1H, NH), 7.45 (d, 2H, Ar, J = 8.1 Hz), 7.79 (d, 2H, Ar, J = 8.1 Hz), 7.84 (s, 1H, NH). ¹³C NMR (75 MHz, CDCl₃): δ 41.3, 53.1, 103.1, 127.3, 128.2, 130.0, 131.3, 134.6, 142.1, 167.5, 168.6. FT-IR (wavenumber, cm⁻¹): 3290 (N–H), 3096 (C–H, alkene), 2947 (C–H, alkyl), 1634 (C=O), 1593 (C=O), 1448 (C=C, aromatic), 1413 (C=C, aromatic). HRMS⁺ C₁₅H₂₁N₂O₄: Theoretical: 293.1501. Actual: 293.1503.

N-Ethylacrylamide-2-(4-formylbenzamide)⁴ (M1):

A solution of *N*-ethylacrylamide-2-(4-(dimethoxymethyl)benzamide) **2** (1.4 g, 4.8 mmol) in 1M $HCl_{(aq)}$ (20 mL) was stirred at room temperature for 2 h then neutralized with saturated NaHCO_{3(aq)} (100 mL). The aqueous layer was extracted with EtOAc (3 × 150 mL). The organic extracts were combined and dried over MgSO₄, filtered and evaporated to dryness to afford the title product as a white solid (0.99g, 84 %). ¹H NMR (300 MHz, DMSO-d₆): δ 3.72 (m, 4H, (CH₂)₂), 5.59 (dd, 1H, J = 9.6 Hz), 6.09 (dd, 1H, J = 17.1 Hz), 6.23 (dd, 1H, J = 17.1 Hz), 7.99 (d, 2H, Ar, J = 8.4 Hz), 8.03 (d, 2H, Ar, J = 8.4 Hz), 8.23 (s, 1H, NH), 8.79 (s, 1H, NH), 10.07 (s, 1H, CHO). ¹³C NMR (75 MHz, DMSO-d₆): δ 38.7, 125.2, 128.3, 129.6, 132.3, 138.2, 140.1, 165.5, 166.1, 193.0. FT-IR (wavenumber, cm⁻¹): 3264 (N–H), 3091 (C–H, alkene), 2943 (C–H, alkyl), 1699 (C=O, aldehyde), 1627 (C=O, amide), 1549 (C=O, amide), 1447 (C=C, aromatic), 1414 (C=C, aromatic). HRMS⁺ C_{13H15}N₂O₃: Theoretical: 247.1083. Actual: 247.1085.



Scheme 2 Synthesis of aldehyde functional copolymer P1.

Aldehyde-Functionalized Copolymer (P1):

S-1-Dodecyl-*S*'-(α,α -dimethyl- α ''-acetic acid)trithiocarbonate⁵ (DDMAT) (1 eq, 25.0 mg, 68.9 µmol) and AIBN (0.2 eq, 2.3 mg, 14 µmol) were added to a small schlenk tube. *N*,*N*'-Dimethylacrylamide (DMA) (80 eq, 0.545 g, 5.50 mmol) and *N*-ethylacrylamide-2-(4-formylbenzamide) (**M1**) (20 eq, 0.363 g, 1.37 mmol) were then added followed by DMF (3 mL). The reaction mixture was degassed

five times, and then the vessel was backfilled with N₂, purged with N₂, and allowed to warm to room temperature. The reaction mixture was then placed in an oil bath at 70 °C, and the polymerization was quenched after 22 h. The reaction mixture was dissolved in a minimal amount of THF and added dropwise to a large excess of ice-cold diethyl ether. The polymer was then isolated by filtration and the precipitation was repeated before drying under high vacuum. Polymer **P1** was obtained as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃): 1.4 - 1.8 (br, CHCH₂, polymer backbone), 2.2 - 2.7 (br, CHCH₂, polymer backbone), 2.88 (br, N(CH₃)₂), 3.4 - 3.6 (br, (CH₂)₂), 7.88 (br, Ar), 8.07 (br, Ar), 8.59 (br, NH), 10.04 (br, Ar). The composition of **P1** can be determined by comparing the integration of the aldehyde protons of **M1** with the integration of the N(CH₃)₂ protons of DMA. The monomer compositions were not determined to identical to the feed ratio of DMA:**M1** as a consequence of the difference in reactivity of the two monomers.



Fig. 2 ¹H NMR spectrum of P1 (500 MHz, CDCl₃).



Fig. 3 Gel permeation chromatography (GPC) refractive index (dRI) trace in DMF + 1 g L^{-1} LiBr (0.6 mL/ min) of **P1**.

Polymer	DDMAT	AIBN /	DMA /	M1 /	n ^a	m ^a	$n:m^a$	M_n^a /	M_n^b /	$M_{ m w}{}^b$ /	PDI^{b}
	/ eq.	eq.	eq.	eq.				gmol ⁻¹	gmol ⁻¹	gmol ⁻¹	$(M_{\rm w}/M_{\rm n})$
P1	1	0.2	80	20	11	66	1:6	9,800	14,100	17,600	1.25

Table 1 Characterisation of copolymer **P1**. ^{*a*} As determined by ¹H NMR spectroscopy ^{*b*} As determined by gel permeation chromatography in DMF + 1 g L⁻¹ LiBr (0.6 mL/ min) calibrated against near monodisperse poly(methyl methacrylate) standards. AIBN: azobis(isobutyronitrile), DMA: *N*,*N*-dimethylacrylamide, DDMAT: *S*-1-dodecyl-*S*'-(α , α -dimethyl- α ''-acetic acid)trithiocarbonate.



Scheme 3 Synthesis of 4-benzoylhydrazide α -D-galactopyranoside (GAL). (i) BF₃.OEt₂, C₂H₄Cl₂, 50 °C, 21 h. (ii) NaOMe, MeOH, 18 h. (iii) N₂H₄.H₂O, MeOH, reflux, 2 h.

4-methoxycarbonylphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (3):

Boron trifluoride diethyl etherate (4.84 mL, 38.4 mmol) was added dropwise to a solution of β -D-galactose pentaacetate (5.00 g, 12.8 mmol) and 4-(methoxycarbonyl)phenol (3.89 g, 25.6 mmol) in dichloroethane (30 mL) at 50°C. The reaction mixture was stirred for a further 21 h at 50°C before quenching by addition of saturated NaHCO_{3(aq)} (30 mL). The organic layer was then separated and washed with NaCl_(aq) (50 mL), dried over MgSO₄, concentrated *in vacuo* and purified by flash column chromoatography (SiO₂, 2:1 hexane:ethyl acetate \rightarrow 1:1 hexane:ethyl acetate) to afford **3** as a mixture of anomers (3.95 g, 64%, α : β 74:26). The mixture was then recrystallized from methanol to afford **3** as colourless plates of only the α -anomer (2.07 g, 46%); m.p. 112-117°C (from methanol); [α]_D²⁵ + 212.7 (*c* 0.22, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, *J* = 8.7 Hz, 2H, Ar), 7.11 (d, *J* = 8.7 Hz, 2H, Ar), 5.86 (d, *J*_{1,2} = 3.6 Hz, 1H, H-1), 5.57 (dd, *J*_{3,2} = 10.9, *J*_{3,4} = 3.6 Hz, 1H, H-3), 5.53 (d, *J*_{4,3} = 3.6 Hz, 1H, H-4), 5.31 (dd, *J*_{2,3} = 10.9, *J*_{2,1} = 3.6 Hz, 1H, H-2), 4.29 (dd, *J*_{5,6} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-6), 4.06 (dd, *J*_{6',6} = 11.2 Hz, *J*_{6',5} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-6), 4.06 (dd, *J*_{6',6} = 11.2 Hz, *J*_{6',5} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-6), 4.06 (dd, *J*_{6',6} = 11.2 Hz, *J*_{6',5} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-6), 4.06 (dd, *J*_{6',6} = 11.2 Hz, *J*_{6',5} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-6), 4.06 (dd, *J*_{6',6} = 11.2 Hz, *J*_{6',5} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-6), 4.06 (dd, *J*_{6',6} = 11.2 Hz, *J*_{6',5} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-5), 4.11 (dd, *J*_{6,6'} = 11.2 Hz, *J*_{6,5} = 6.6 Hz, 1H, H-6), 4.06 (dd, *J*_{6',6} = 11.2 Hz,

H6'), 3.90 (s, 3H, OMe), 2.18 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.93 (s, 3H, OAc). ¹³C NMR (75 MHz, CDCl₃): δ 170.39, 170.28, 170.14, 170.03, 166.47 (C=O), 159.70, 131.59, 124.77, 116.13, (ArC), 94.45 (C-1), 67.71, 67.54, 67.47, 67.37 (C-2, C-3, C-4, C-5), 61.39 (C-6), 52.07 (OCH₃), 20.75, 20.68, 20.64, 20.58 (COCH₃). HRESIMS: Found [M+Na]⁺ 505.1314, C₂₂H₂₆O₁₂Na requires 505.1316; IR (v_{max}/cm⁻¹) 1751 (C=O).

4-Methoxycarbonylphenyl α-D-galactopyranoside (4):

Sodium methoxide (150 mg, 2.79 mmol) was added to a solution of 4-methoxycarbonylphenyl 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranoside **3** (1.68 g, 3.49 mmol) in anhydrous methanol (30 mL), after stirring for 18 h a r.t. the reaction mixture was neutralised with amberlite IRC 50 H⁺ resin, filtered and concentrated to afford **4** (889 mg, 82%) as a colourless glassy solid; $[\alpha]_D^{25}$ +231.8 (*c* 0.17, H₂O); ¹H NMR (500 MHz, MeOD) δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 5.65 (d, *J*_{1,2} = 2.8 Hz, 1H, H-1), 4.00 (m, 3H, H-2, H-3, H-4), 3.90 (s, 3H, OMe), 3.87 (m, 1H, H-5), 3.70 (m, 2H, H-6, H6'); ¹³C NMR (75 MHz, MeOD) δ 168.29 (C=O), 162.66, 132.40, 124.94, 117.62 (ArC), 99.26 (C-1), 73.56, 71.27, 70.71, 69.78 (C-2, C-3, C-4, C-5), 62.39 (C-6), 52.45 (OCH₃); HRESIMS: Found [M+Na]⁺ 337.0888, C₁₄H₁₈O₈Na requires 337.0894.

4-Benzoylhydrazide α-D-galactopyranoside (GAL):

Hydrazine monohydrate (719 μL, 14.8 mmol) was added to a solution of 4-methoxycarbonylphenyl α-D-galactopyranoside **4** (230 mg, 0.79 mmol) in methanol (3 mL) and heated at reflux for 2 h, over the course of which a colourless solid precipitated. The solid was filtered and lyophilized from water to afford **GAL** (170 mg, 74%) as colourless lyophilisate; $[\alpha]_D^{25}$ +141.0 (*c* 0.2, H₂O); ¹H NMR (500 MHz, D₂O) δ 7.67 (d, *J* = 8.0 Hz, 2H, ArH), 7.19 (d, *J* = 8.0 Hz, 2H, ArH), 5.71 (d, *J*_{1,2} = 3.8 Hz, 1H, H-1), 4.04 (dd, *J*_{3,2} = 9.8 Hz, *J*_{3,4} = 4.3 Hz, 1H, H-3), 3.98 (d, *J* = 4.3 Hz, 1H, H-4), 3.94 (m, 2H, H,-2, H-6), 3.66 – 3.59 (m, 2H, H-5, H-6'); ¹³C NMR (75 MHz, D₂O) δ 158.96, (<u>C</u>ONHNH₂), 128.84, 126.16, 124.11, 116.73 (ArC), 96.63 (C-1), 71.81, 69.29, 68.98, 67.87(C-2, C-3, C-4, C-5) 60.88 (C-6); *J*_{C1-H1} = 190.00 Hz (consistent with α-configuration);⁶ HRESIMS: Found [M+Na]⁺ 337.1015, C₁₃H₁₈N₂NaO₇ requires 337.1015.



Scheme 4 Synthesis of 4-benzoylhydrazide α -D-mannopyranoside (**MAN**). (i) BF₃.OEt₂, C₂H₄Cl₂, 50 °C, 24 h. (ii) NaOMe, MeOH, 18 h. (iii) N₂H₄.H₂O, MeOH, reflux, 4 h.

4-Methoxycarbonylphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (5):

Boron trifluoride diethyl etherate (4.84 mL, 38.4 mmol) was added dropwise to a solution of β -D-mannose pentaacetate (5 g, 12.8 mmol) and 4-(methoxycarbonyl)phenol (3.89 g, 25.6 mmol) in dichloroethane (30 mL) at 50 °C. The reaction mixture was stirred for a further 24 h at 50 °C before quenching by addition of aq. NaHCO₃ (30 mL). The organic layer was then separated and washed with aq. NaCl (50 mL), dried (MgSO₄), concentrated and purified by flash silica column chromatography (2:1 hexane-ethyl acetate \rightarrow 1:1 hexane-ethyl acetate) and the semi-crude product recrystallised from methanol to afford **5** (2.72 g, 44%) as colourless plates; m.p. 137-140 °C (from

methanol); $[\alpha]_{D}^{25}$ +88.8 (*c* 0.65, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 5.60 (d, *J*_{1,2} = 1.8 Hz, 1H, H-1), 5.55 (dd, *J*_{3,4} = 10.0 Hz, *J*_{3,2} = 3.5 Hz, 1H, H-3), 5.46 (dd, *J*_{2,3} = 3.5 Hz, *J*_{2,1} = 1.8 Hz, 1H, H-2), 5.37 (t, *J*_{4,3} = 10.2 Hz, *J*_{4,5} = 10.2 Hz, 1H, H-4), 4.28 (dd, *J*_{6,6'} = 12.3 Hz, *J*_{5,6} = 5.6 Hz, 1H, H-6), 4.09 – 4.02 (m, 2H, H-5, H-6'), 3.90 (s, 3H, OMe), 2.21 (s, 3H, COCH₃), 2.06 (s, 3H, COCH₃), 2.04 (s, 3H, COCH₃), 2.02 (s, 3H, COCH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.48, 169.95, 169.69, 166.44 (C=O), 158.99, 131.60, 124.84, 115.94 (ArC), 95.41 (C-1), 69.41, 69.14, 68.68, 65.73, 61.98 (C-6), 52.07 (OCH₃), 20.87, 20.70, 20.69, 20.67 (CO<u>C</u>H₃); HRESIMS: Found [M+Na]⁺ 505.1316, C₂₂H₂₆O₁₂Na requires 505.1316; IR (v_{max}/cm⁻¹) 1751 (C=O).

4-Methoxycarbonylphenyl α-D-mannopyranoside (6):⁷

Sodium methoxide (92 mg, 1.70 mmol) was added to a solution of 4-methoxycarbonylphenyl 2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranoside **5** (1.027 g, 2.13 mmol) in anhydrous methanol (20 mL), after stirring for 18 h a r.t. the reaction mixture was neutralised with amberlite IRC 50 H⁺ resin, filtered and concentrated to afford **6** (622 mg, 93%) as a colourless glassy solid; $[\alpha]_D^{25}$ +60.1 (*c* 0.8, H₂O); ¹H NMR (500 MHz, D₂O) δ 7.92 (d, *J* = 7.5 Hz, 2H, ArH), 7.15 (d, *J* = 7.5 Hz, 2H, ArH), 5.65 (d, *J*_{1,2} = 1.8 Hz, 1H, H-1), 4.11 (dd, *J*_{2,3} = 3.1 Hz, *J*_{2,1} = 1.8 Hz, 1H, H-2), 3.99 (dd, *J*_{3,4} = 9.7 Hz, *J*_{3,2} = 3.1 Hz, 1H, H-3), 3.83 (s, 3H, OCH₃), 3.72 – 3.63 (m, 3H, H-4, H-6, H-6'), 3.59 – 3.56 (m, 1H, H-5); ¹³C NMR (75 MHz, D₂O) δ 168.91 (C=O), 159.47, 131.45, 123.40, 116.26 (ArC), 97.43 (C-1), 73.41, 70.22, 69.63, 66.39 (C-2, C-3, C-4, C-5), 60.51 (C-6), 52.37 (OCH₃).

4-Benzoylhydrazide α-D-mannopyranoside (MAN):

Hydrazine monohydrate (719 μL, 14.8 mmol) was added to a solution of 4-methoxycarbonylphenyl α-D-mannopyranoside **6** (230 mg, 0.79 mmol) in methanol (3 mL) and heated at reflux for 4 h. The solution was then concentrated and lyophilized from water to afford **MAN** (225 mg, 98%) as a colourless lyophilisate $[\alpha]_D^{25}$ +94.2 (*c* 0.52, H₂O); ¹H NMR (500 MHz, MeOD) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 5.61 (d, *J*_{1,2} = 1.8 Hz, 1H, H-1), 4.06 (dd, *J*_{2,3} = 3.5 Hz, *J*_{2,1} = 1.8 Hz, 1H, H-2), 3.95 (dd, *J*_{3,4} = 9.5 Hz, *J*_{3,2} = 3.5 Hz, 1H), 3.84 – 3.71 (m, 3H, H-4, H-6, H-6'), 3.59 (ddd, *J*_{5,4} = 9.8 Hz, *J*_{5,6} = 5.3 Hz, *J*_{5,6'} = 2.6 Hz, 1H, H-5); ¹³C NMR (125 MHz, MeOD) δ 169.33 (CONHNH₂), 160.61, 130.02, 127.98, 117.46 (ArC), 100.00 (C-1), 75.71 (C-5), 72.43 (C-3), 71.89 (C-2), 68.34 (C-4), 62.70 (C-6); *J*_{C1-H1} = 171.00 Hz (consistent with α-configuration);⁸ HRESIMS: Found [M+H]⁺ 315.1189, C₁₃H₁₉N₂O₇ requires 315.1189.

General Procedure for Preparation of Polymers with Fixed Carbohydrate Compositions

PS-DCLs were prepared so as to contain 25 mM concentrations of acylhydrazides **GAL** and **MAN**, with polymer **P1** present at a concentration of 1.85 mM (i.e. effective concentration of aldehyde functionalities is 20.3 mM).

Polymer P1 was combined with galactosyl derivative GAL in 0.1 M NH₄OAc/AcOH deuterated buffer (pH 4.5, 0.5 mL) and sonicated until a clear solution was obtained. Mannosyl derivative MAN was added to the reaction mixture, which was left overnight to equilibrate. Equilibration to the required ratio of GAL and MAN was confirmed by ¹H NMR spectroscopic analysis prior to reduction. NaCNBH₃ (10 eq. per aldehyde functionality) was added to the solution and the reaction mixture was left overnight at room temperature. Reduction was confirmed by ¹H NMR spectroscopic analysis prior to dialysis against H₂O and lyophilisation to yield polymer libraries UT, P-MAN and P-GAL.

General Procedure for Lectin Functionalisation of 96-well plates

Wells were washed with D_2O (200 µL) before treatment with solution of biotinylated lectin (3.0 mg biotinyl-Con A/3000 µL D_2O , 0.25 mg biotinyl-LTB/3000 µL 100 mM NaCl, D_2O) (100 µL). Plates were incubated at 5 °C for 16 h before lectin solutions were removed and wells were washed with 100 mM NH₄OAc/AcOH deuterated buffer pH 4.5 before addition of PS-DCLs.

General Procedure for Isolation of Library Members from Lectin-functionalised Wells

The bulk of the PS-DCL was pipetted from the wells, and the surfaces of the wells were incubated for 1 h with a denaturant solution (50 mM EDTA in D₂O in the case of Con A, and 5.0 M guanidinium chloride, 0.5 M NaCl in D₂O in the case of LTB) (100 μ L per well). ¹H NMR spectroscopic analysis revealed both sets of washings to contain polymeric species which were purified by dialysis then lyophilised to yield **T-Con A** or **T-LTB**. Concentration of glycopolymers in material isolated from the wells was determined based on the absorbance of glycopolymers at 310 nm.

Beer-Lambert Analysis of Glycopolymers:



Fig. 4 (a) UV-Visible spectra of solutions of UT in the range 0 μ M to 5.00 μ M. (b) Beer-Lambert plot for UT.

Solutions of **UT** of known concentrations between 0 μ M and 5.00 μ M were prepared and their absorbance at 310 nm was determined (Fig. 4), allowing the molar extinction coefficient ε_{310} to be determined to be 0.264 μ M⁻¹ cm⁻¹.

General Procedure for Fluorescence Titrations

Solutions of Con A and LTB were prepared at 0.5 μ M concentrations. Solutions of polymers were prepared by dissolving the polymer in the appropriate lectin solution to ensure a constant concentration of lectin throughout the titration. The lectin solution (400 μ L) was placed in a cuvette and the appropriate polymer solution was added in small aliquots (5.0 μ L). The samples were excited at a wavelength of 280 nm and the change in emission intensity at 340 nm was recorded. Control experiments were performed where solutions of polymers were titrated into a solution of the buffer in the absence of lectin. The change in intensity of fluorescence of the solution as a consequence of polymer addition was monitored, and these values were subtracted from those obtained during titrations of polymers with lectins.

Binding stoichiometries (*n*) were determined by Job Plot analysis. Dissociation constants were calculated using non-linear regression methods, with data fitted to a modified Hill equation $y = V_{max}$

 $\frac{x^n}{K_d^n + x^n}$. The binding stoichiometry *n* was obtained from the relevant Job Plot. This analysis yielded values of *n* between 0.8 and 1.2 for each set of polymers investigated. While the apparent binding stoichiometries of polymers with templates may not be identical, we believe that they are sufficiently similar, reflecting comparable modes of binding and thus allow for direct comparison of K_a values.

Binding Curves

Polymer mixture **T-Con A** vs. Con A (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 2 mM CaCl₂.

[ConA] / M	[T-Con A] / M	[T-Con A]/[Con A]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	27033840	0
5.00 x 10 ⁻⁷	2.78 x 10 ⁻⁸	0.06	25962039	1071801
5.00 x 10 ⁻⁷	5.52 x 10 ⁻⁸	0.12	24622579	2411261
5.00 x 10 ⁻⁷	8.24 x 10 ⁻⁸	0.16	23918500	3115340
5.00 x 10 ⁻⁷	1.09 x 10 ⁻⁷	0.22	23290152	3743688
5.00 x 10 ⁻⁷	1.36 x 10 ⁻⁷	0.28	22683587	4350253
5.00 x 10 ⁻⁷	1.62 x 10 ⁻⁷	0.32	21884039	5149801
5.00 x 10 ⁻⁷	1.88 x 10 ⁻⁷	0.38	21413895	5619945
5.00 x 10 ⁻⁷	2.13 x 10 ⁻⁷	0.42	20971402	6062438
5.00 x 10 ⁻⁷	2.39 x 10 ⁻⁷	0.48	20545434	6488406
5.00 x 10 ⁻⁷	2.64 x 10 ⁻⁷	0.52	20278383	6755457
5.00 x 10 ⁻⁷	2.89 x 10 ⁻⁷	0.58	19515794	7518046
5.00 x 10 ⁻⁷	3.13 x 10 ⁻⁷	0.62	19093892	7939948
5.00 x 10 ⁻⁷	3.37 x 10 ⁻⁷	0.68	18972708	8061132
5.00 x 10 ⁻⁷	3.61 x 10 ⁻⁷	0.72	18600580	8433260
5.00 x 10 ⁻⁷	3.85 x 10 ⁻⁷	0.78	18187090	8846750
5.00 x 10 ⁻⁷	4.09 x 10 ⁻⁷	0.82	17886671	9147169
5.00 x 10 ⁻⁷	4.32 x 10 ⁻⁷	0.86	17671436	9362404
5.00 x 10 ⁻⁷	4.55 x 10 ⁻⁷	0.90	17260411	9773429
5.00 x 10 ⁻⁷	4.78 x 10 ⁻⁷	0.96	17015640	10018200
5.00 x 10 ⁻⁷	5.00 x 10 ⁻⁷	1.00	16895578	10138262



 $K_{\rm a} = 3.76 \text{ x } 10^6 \pm 2.26 \text{ x } 10^5 \text{ M}^{-1}$ n = 1.2

Polymer mixture **UT** vs. Con A (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 2 mM CaCl₂.

[ConA] / M		[UT] / M	[UT]/[ConA]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
	5.00 x 10 ⁻⁷	0	0.00	24911023	0
4	5.00 x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.29	23960979	950044
4	5.00 x 10 ⁻⁷	2.91 x 10 ⁻⁷	0.58	22126679	2784344
	5.00 x 10 ⁻⁷	4.34 x 10 ⁻⁷	0.87	20639898	4271125
4	5.00 x 10 ⁻⁷	5.75 x 10 ⁻⁷	1.15	19112721	5798302
4	5.00 x 10 ⁻⁷	7.14 x 10 ⁻⁷	1.43	18225714	6685309
4	5.00 x 10 ⁻⁷	8.52 x 10 ⁻⁷	1.70	17809433	7101590
4	5.00 x 10 ⁻⁷	9.89 x 10 ⁻⁷	1.98	16679502	8231521
4	5.00 x 10 ⁻⁷	1.12 x 10 ⁻⁶	2.25	16363181	8547842
4	5.00 x 10 ⁻⁷	1.26 x 10 ⁻⁶	2.51	15621715	9289308
	5.00 x 10 ⁻⁷	1.39 x 10 ⁻⁶	2.78	15008760	9902263
4	5.00 x 10 ⁻⁷	1.52 x 10 ⁻⁶	3.04	14317076	10593947
	5.00 x 10 ⁻⁷	1.65 x 10 ⁻⁶	3.30	13913730	10997293
4	5.00 x 10 ⁻⁷	1.78 x 10 ⁻⁶	3.55	13112271	11798752
4	5.00 x 10 ⁻⁷	1.90 x 10 ⁻⁶	3.80	12844170	12066853
	5.00 x 10 ⁻⁷	2.03 x 10 ⁻⁶	4.05	12421210	12489813
	5.00 x 10 ⁻⁷	2.15 x 10 ⁻⁶	4.30	12066864	12844159
4	5.00 x 10 ⁻⁷	2.27 x 10 ⁻⁶	4.55	11555018	13356005
4	5.00 x 10 ⁻⁷	2.39 x 10 ⁻⁶	4.79	11272457	13638566
4	5.00 x 10 ⁻⁷	2.51 x 10 ⁻⁶	5.03	10932849	13978174
	5.00 x 10 ⁻⁷	2.63 x 10 ⁻⁶	5.26	10922158	13988865



$$K_{\rm a} = 4.45 \text{ x } 10^5 \pm 2.64 \text{ x } 10^4 \text{ M}^{-1}$$

 $n = 1.0$

[ConA] / M	[TC-Con A] / M	[TC-Con A]/[ConA]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	29025026	0
5.00 x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.29	27504128	1520898
5.00 x 10 ⁻⁷	2.91 x 10 ⁻⁷	0.58	26101405	2923621
5.00 x 10 ⁻⁷	4.34 x 10 ⁻⁷	0.87	25298087	3726939
5.00 x 10 ⁻⁷	5.75 x 10 ⁻⁷	1.15	23691479	5333547
5.00 x 10 ⁻⁷	7.14 x 10 ⁻⁷	1.43	22780636	6244390
5.00 x 10 ⁻⁷	8.52 x 10 ⁻⁷	1.70	21988201	7036825
5.00 x 10 ⁻⁷	9.89 x 10 ⁻⁷	1.98	21215624	7809402
5.00 x 10 ⁻⁷	1.12 x 10 ⁻⁶	2.25	20470931	8554095
5.00 x 10 ⁻⁷	1.26 x 10 ⁻⁶	2.51	19556882	9468144
5.00 x 10 ⁻⁷	1.39 x 10 ⁻⁶	2.78	18792290	10232736
5.00 x 10 ⁻⁷	1.52 x 10 ⁻⁶	3.04	18197167	10827859
5.00 x 10 ⁻⁷	1.65 x 10 ⁻⁶	3.30	17488722	11536304
5.00 x 10 ⁻⁷	1.78 x 10 ⁻⁶	3.55	16974468	12050558
5.00 x 10 ⁻⁷	1.90 x 10 ⁻⁶	3.80	16388004	12637022
5.00 x 10 ⁻⁷	2.03 x 10 ⁻⁶	4.05	15912844	13112182
5.00 x 10 ⁻⁷	2.15 x 10 ⁻⁶	4.30	15344856	13680170
5.00 x 10 ⁻⁷	2.27 x 10 ⁻⁶	4.55	14852847	14172179
5.00 x 10 ⁻⁷	2.39 x 10 ⁻⁶	4.79	14597449	14427577
5.00 x 10 ⁻⁷	2.51 x 10 ⁻⁶	5.03	14098280	14926746
5.00 x 10 ⁻⁷	2.63 x 10 ⁻⁶	5.26	13661568	15363458

Polymer mixture **TC-Con A** vs. Con A (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 2 mM CaCl₂.







Polymer mixture **P-MAN** vs. Con A (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 2 mM CaCl₂.

[Con A] / M	[P-MAN]/M	[P-MAN]/[Con A]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	25735132	0
5.00 x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.29	24243899	1491233
5.00 x 10 ⁻⁷	2.91 x 10 ⁻⁷	0.58	23387902	2347230
5.00 x 10 ⁻⁷	4.34 x 10 ⁻⁷	0.87	22763213	2971919
5.00 x 10 ⁻⁷	5.75 x 10 ⁻⁷	1.15	22112881	3622251
5.00 x 10 ⁻⁷	7.14 x 10 ⁻⁷	1.43	21395186	4339946
5.00 x 10 ⁻⁷	8.52 x 10 ⁻⁷	1.70	20758873	4976259
5.00 x 10 ⁻⁷	9.89 x 10 ⁻⁷	1.98	20304307	5430825
5.00 x 10 ⁻⁷	1.12 x 10 ⁻⁶	2.25	19844872	5890260
5.00 x 10 ⁻⁷	1.26 x 10 ⁻⁶	2.51	19537970	6197162
5.00 x 10 ⁻⁷	1.39 x 10 ⁻⁶	2.78	19022190	6712942
5.00 x 10 ⁻⁷	1.52 x 10 ⁻⁶	3.04	18637008	7098124
5.00 x 10 ⁻⁷	1.65 x 10 ⁻⁶	3.30	18120742	7614390
5.00 x 10 ⁻⁷	1.78 x 10 ⁻⁶	3.55	17853377	7881755



$$K_{\rm a} = 5.26 \text{ x } 10^5 \pm 4.77 \text{ x } 10^4 \text{ M}^{-1}$$

 $n = 1.0$

Polymer mixture **P-GAL** vs. Con A (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 2 mM CaCl₂.

[ConA] / M		[L5]/M	[L5]/[ConA]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00	x 10 ⁻⁷	0	0.00	21696619	0
5.00	x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.29	19948963	1747656
5.00	x 10 ⁻⁷	2.91 x 10 ⁻⁷	0.58	18799701	2896918
5.00	x 10 ⁻⁷	4.34 x 10 ⁻⁷	0.87	17754174	3942445
5.00	x 10 ⁻⁷	5.75 x 10 ⁻⁷	1.15	17156181	4540438
5.00) x 10 ⁻⁷	7.14 x 10 ⁻⁷	1.43	16398500	5298119
5.00) x 10 ⁻⁷	8.52 x 10 ⁻⁷	1.70	15667055	6029564
5.00	x 10 ⁻⁷	9.89 x 10 ⁻⁷	1.98	15179674	6516945
5.00	x 10 ⁻⁷	1.12 x 10 ⁻⁶	2.25	14713588	6983031
5.00	x 10 ⁻⁷	1.26 x 10 ⁻⁶	2.51	14074958	7621661
5.00	x 10 ⁻⁷	1.39 x 10 ⁻⁶	2.78	13483935	8212684
5.00	x 10 ⁻⁷	1.52 x 10 ⁻⁶	3.04	13018135	8678484
5.00	x 10 ⁻⁷	1.65 x 10 ⁻⁶	3.30	12568757	9127862
5.00	x 10 ⁻⁷	1.78 x 10 ⁻⁶	3.55	11986834	9709785
5.00) x 10 ⁻⁷	1.90 x 10 ⁻⁶	3.80	11569362	10127257
5.00	x 10 ⁻⁷	2.03 x 10 ⁻⁶	4.05	11092850	10603769



$$K_{\rm a} = 4.66 \pm 1.12 \text{ x } 10^4 \text{ M}^{-1}$$

n = 0.7

[LTB]/M	[T-LTB]/M	[T-LTB]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	20691937	0
5.00 x 10 ⁻⁷	6.16 x 10 ⁻⁸	0.12	20115232	576705
5.00 x 10 ⁻⁷	1.23 x 10 ⁻⁷	0.25	19571118	1120819
5.00 x 10 ⁻⁷	1.84 x 10 ⁻⁷	0.37	19009529	1682408
5.00 x 10 ⁻⁷	2.45 x 10 ⁻⁷	0.49	18583273	2108664
5.00 x 10 ⁻⁷	3.06 x 10 ⁻⁷	0.61	18361410	2330527
5.00 x 10 ⁻⁷	3.67 x 10 ⁻⁷	0.73	17831302	2860635
5.00 x 10 ⁻⁷	4.28 x 10 ⁻⁷	0.86	17558538	3133399
5.00 x 10 ⁻⁷	4.88 x 10 ⁻⁷	0.98	17164256	3527681
5.00 x 10 ⁻⁷	5.49 x 10 ⁻⁷	1.10	16822796	3869141
5.00 x 10 ⁻⁷	6.09 x 10 ⁻⁷	1.22	16629690	4062247
5.00 x 10 ⁻⁷	6.69 x 10 ⁻⁷	1.34	16408350	4283587
5.00 x 10 ⁻⁷	7.29 x 10 ⁻⁷	1.46	16217030	4474907
5.00 x 10 ⁻⁷	7.89 x 10 ⁻⁷	1.58	16082529	4609408
5.00 x 10 ⁻⁷	8.48 x 10 ⁻⁷	1.70	15860147	4831790
5.00 x 10 ⁻⁷	9.08 x 10 ⁻⁷	1.82	15679638	5012299
5.00 x 10 ⁻⁷	9.67 x 10 ⁻⁷	1.93	15436391	5255546
5.00 x 10 ⁻⁷	1.03 x 10 ⁻⁶	2.05	15222046	5469891

Polymer mixture **T-LTB** vs. LTB (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 100 mM NaCl.



$$K_{\rm a} = 1.74 \text{ x } 10^6 \pm 6.97 \text{ x } 10^4 \text{ M}^{-1}$$

 $n = 0.8$

Polymer mixture **UT** vs. LTB (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 100 mM NaCl.

[LTB]/M	[UT] / M	[UT]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	22164883	0
5.00 x 10 ⁻⁷	5.92 x 10 ⁻⁷	1.18	20856802	1308081
5.00 x 10 ⁻⁷	1.18 x 10 ⁻⁶	2.36	19923931	2240952
5.00 x 10 ⁻⁷	1.77 x 10 ⁻⁶	3.54	19059505	3105378
5.00 x 10 ⁻⁷	2.35 x 10 ⁻⁶	4.70	18696704	3468179
5.00 x 10 ⁻⁷	2.93 x 10 ⁻⁶	5.86	17883253	4281630
5.00 x 10 ⁻⁷	3.51 x 10 ⁻⁶	7.02	17206184	4958699
5.00 x 10 ⁻⁷	4.08 x 10 ⁻⁶	8.17	16786880	5378003
5.00 x 10 ⁻⁷	4.66 x 10 ⁻⁶	9.31	16459046	5705837
5.00 x 10 ⁻⁷	5.23 x 10 ⁻⁶	10.5	15869460	6295423
5.00 x 10 ⁻⁷	5.79 x 10 ⁻⁶	11.6	15740215	6424668



$$K_{\rm a} = 1.68 \text{ x } 10^5 \pm 1.69 \text{ x } 10^4 \text{ M}^{-1}$$

 $n = 1.0$

[LTB]/M	[TC-LTB]/M	[TC-LTB]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	16867283	0
5.00 x 10 ⁻⁷	1.86 x 10 ⁻⁷	0.37	14521991	2345292
5.00 x 10 ⁻⁷	3.68 x 10 ⁻⁷	0.74	13559240	3308043
5.00 x 10 ⁻⁷	5.46 x 10 ⁻⁷	1.09	12426922	4440361
5.00 x 10 ⁻⁷	7.21 x 10 ⁻⁷	1.44	11852483	5014800
5.00 x 10 ⁻⁷	8.93 x 10 ⁻⁷	1.79	10905436	5961847
5.00 x 10 ⁻⁷	1.06 x 10 ⁻⁶	2.12	10499772	6367511
5.00 x 10 ⁻⁷	1.23 x 10 ⁻⁶	2.45	9801183	7066100
5.00 x 10 ⁻⁷	1.39 x 10 ⁻⁶	2.78	9340755	7526528
5.00 x 10 ⁻⁷	1.55 x 10 ⁻⁶	3.10	9111654	7755629
5.00 x 10 ⁻⁷	1.70 x 10 ⁻⁶	3.41	8782440	8084843
5.00 x 10 ⁻⁷	1.86 x 10 ⁻⁶	3.72	8499104	8368179
5.00 x 10 ⁻⁷	2.01 x 10 ⁻⁶	4.02	8202676	8664607
5.00 x 10 ⁻⁷	2.16 x 10 ⁻⁶	4.31	7694166	9173117
5.00 x 10 ⁻⁷	2.30 x 10 ⁻⁶	4.61	7411897	9455386
5.00 x 10 ⁻⁷	2.45 x 10 ⁻⁶	4.89	7190938	9676345
5.00 x 10 ⁻⁷	2.59 x 10 ⁻⁶	5.17	6855491	10011792
5.00 x 10 ⁻⁷	2.72 x 10 ⁻⁶	5.45	6522955	10344328
5.00 x 10 ⁻⁷	2.86 x 10 ⁻⁶	5.72	6324065	10543218
5.00 x 10 ⁻⁷	2.99 x 10 ⁻⁶	5.99	6065189	10802094
5.00 x 10 ⁻⁷	3.13 x 10 ⁻⁶	6.25	5585472	11281811

Polymer mixture **TC-LTB** vs. LTB (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 100 mM NaCl.





$$K_a = 6.27 \text{ x } 10^5 \pm 5.05 \text{ x } 10^4 \text{ M}^{-1}$$

 $n = 1.0$

[LTB] / M	[L4]/M	[L4]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	20303483	0
5.00 x 10 ⁻⁷	2.97 x 10 ⁻⁷	0.59	19503968	799515
5.00 x 10 ⁻⁷	5.92 x 10 ⁻⁷	1.18	19083764	1219719
5.00 x 10 ⁻⁷	8.87 x 10 ⁻⁷	1.77	18528216	1775267
5.00 x 10 ⁻⁷	1.18 x 10 ⁻⁶	2.36	18181802	2121681
5.00 x 10 ⁻⁷	1.48 x 10 ⁻⁶	2.95	17936194	2367289
5.00 x 10 ⁻⁷	1.77 x 10 ⁻⁶	3.54	17650519	2652964
5.00 x 10 ⁻⁷	2.06 x 10 ⁻⁶	4.12	17336033	2967450
5.00 x 10 ⁻⁷	2.35 x 10 ⁻⁶	4.70	16883891	3419592
5.00 x 10 ⁻⁷	2.64 x 10 ⁻⁶	5.28	16740494	3562989
5.00 x 10 ⁻⁷	2.93 x 10 ⁻⁶	5.86	16359046	3944437
5.00 x 10 ⁻⁷	3.22 x 10 ⁻⁶	6.44	16174128	4129355
5.00 x 10 ⁻⁷	3.51 x 10 ⁻⁶	7.02	15918091	4385392
5.00 x 10 ⁻⁷	3.80 x 10 ⁻⁶	7.60	15671554	4631929
5.00 x 10 ⁻⁷	4.08 x 10 ⁻⁶	8.17	15256107	5047376
5.00 x 10 ⁻⁷	4.37 x 10 ⁻⁶	8.74	14920257	5383226
5.00 x 10 ⁻⁷	4.66 x 10 ⁻⁶	9.31	14707362	5596121
5.00 x 10 ⁻⁷	4.94 x 10 ⁻⁶	9.88	14481955	5821528
5.00 x 10 ⁻⁷	5.23 x 10 ⁻⁶	10.5	14245699	6057784
5.00 x 10 ⁻⁷	5.51 x 10 ⁻⁶	11.0	14094336	6209147
5.00 x 10 ⁻⁷	5.79 x 10 ⁻⁶	11.6	13818802	6484681

Polymer mixture **P-MAN** vs. LTB (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 100 mM NaCl.





 $K_{\rm a} = 1.06 \pm 985.8 \ {
m M}^{-1}$ n = 0.8

[LTB] / M	[P-GAL]/M	[P-GAL]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	20474226	0
5.00 x 10 ⁻⁷	2.97 x 10 ⁻⁷	0.59	20264918	209308
5.00 x 10 ⁻⁷	5.92 x 10 ⁻⁷	1.18	19581988	892238
5.00 x 10 ⁻⁷	8.87 x 10 ⁻⁷	1.77	18919642	1554584
5.00 x 10 ⁻⁷	1.18 x 10 ⁻⁶	2.36	18264098	2210128
5.00 x 10 ⁻⁷	1.48 x 10 ⁻⁶	2.95	17478161	2996065
5.00 x 10 ⁻⁷	1.77 x 10 ⁻⁶	3.54	16636589	3837637
5.00 x 10 ⁻⁷	2.06 x 10 ⁻⁶	4.12	16011452	4462774
5.00 x 10 ⁻⁷	2.35 x 10 ⁻⁶	4.70	15528517	4945709
5.00 x 10 ⁻⁷	2.64 x 10 ⁻⁶	5.28	15003323	5470903
5.00 x 10 ⁻⁷	2.93 x 10 ⁻⁶	5.86	14154199	6320027
5.00 x 10 ⁻⁷	3.22 x 10 ⁻⁶	6.44	13905832	6568394
5.00 x 10 ⁻⁷	3.51 x 10 ⁻⁶	7.02	13213927	7260299
5.00 x 10 ⁻⁷	3.80 x 10 ⁻⁶	7.60	12857599	7616627
5.00 x 10 ⁻⁷	4.08 x 10 ⁻⁶	8.17	12006866	8467360
5.00 x 10 ⁻⁷	4.37 x 10 ⁻⁶	8.74	11627804	8846422
5.00 x 10 ⁻⁷	4.66 x 10 ⁻⁶	9.31	11252340	9221886
5.00 x 10 ⁻⁷	4.94 x 10 ⁻⁶	9.88	11017429	9456797
5.00 x 10 ⁻⁷	5.23 x 10 ⁻⁶	10.5	10796591	9677635
5.00 x 10 ⁻⁷	5.51 x 10 ⁻⁶	11.0	10333571	10140655
5.00 x 10 ⁻⁷	5.79 x 10 ⁻⁶	11.6	10042490	10431736

Polymer mixture **P-GAL** vs. LTB (c.p.s.: counts per second). 100 mM NH₄OAc/AcOH, pH 4.5, 100 mM NaCl.



$$K_{\rm a} = 2.42 \text{ x } 10^5 \pm 4.83 \text{ x } 10^3 \text{ M}^{-1}$$

 $n = 0.8$

[ConA] / M	[T-Con A] / M	[T-Con A]/[ConA]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
2.50 x 10 ⁻⁷	0	0.00	33537753	0
2.50 x 10 ⁻⁷	2.78 x 10 ⁻⁸	0.11	30068554	3469199
2.50 x 10 ⁻⁷	5.52 x 10 ⁻⁸	0.22	26241458	7296295
2.50 x 10 ⁻⁷	8.24 x 10 ⁻⁸	0.33	24390126	9147627
2.50 x 10 ⁻⁷	1.09 x 10 ⁻⁷	0.44	22168268	11369485
2.50 x 10 ⁻⁷	1.36 x 10 ⁻⁷	0.54	20890562	12647191
2.50 x 10 ⁻⁷	1.62 x 10 ⁻⁷	0.65	20194065	13343688
2.50 x 10 ⁻⁷	1.88 x 10 ⁻⁷	0.75	19487524	14050229
2.50 x 10 ⁻⁷	2.13 x 10 ⁻⁷	0.85	18623845	14913908
2.50 x 10 ⁻⁷	2.39 x 10 ⁻⁷	0.96	18044334	15493419
2.50 x 10 ⁻⁷	2.64 x 10 ⁻⁷	1.06	17402147	16135606
2.50 x 10 ⁻⁷	2.89 x 10 ⁻⁷	1.15	16841244	16696509
2.50 x 10 ⁻⁷	3.13 x 10 ⁻⁷	1.25	16420559	17117194
2.50 x 10 ⁻⁷	3.37 x 10 ⁻⁷	1.35	15787595	17750158
2.50 x 10 ⁻⁷	3.61 x 10 ⁻⁷	1.45	15282265	18255488
2.50 x 10 ⁻⁷	3.85 x 10 ⁻⁷	1.54	14778900	18758853
2.50 x 10 ⁻⁷	4.09 x 10 ⁻⁷	1.63	14239588	19298165
2.50 x 10 ⁻⁷	4.32 x 10 ⁻⁷	1.73	13881632	19656121
2.50×10^{-7}	4.55 x 10 ⁻⁷	1.82	13408219	20129534
2.50 x 10 ⁻⁷	4.78 x 10 ⁻⁷	1.91	13045367	20492386
2.50 x 10 ⁻⁷	5.00 x 10 ⁻⁷	2.00	12651944	20885809

Polymer mixture **T-Con A** vs. Con A (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 1 mM MnCl₂.



$$K_{\rm a} = 7.69 \text{ x } 10^6 \pm 4.63 \text{ x } 10^5 \text{ M}^{-1}$$

n = 0.8

[Con A] / M	[UT] / M	[UT]/[Con A]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
2.50 x 10 ⁻⁷	0	0.00	25865657	0
2.50 x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.58	27741925	31494461
2.50 x 10 ⁻⁷	2.91 x 10 ⁻⁷	1.16	25206491	28959027
2.50 x 10 ⁻⁷	4.34 x 10 ⁻⁷	1.73	23997704	27750240
2.50 x 10 ⁻⁷	5.75 x 10 ⁻⁷	2.30	22686388	26438924
2.50 x 10 ⁻⁷	7.14 x 10 ⁻⁷	2.86	21075193	24827729
2.50 x 10 ⁻⁷	8.52 x 10 ⁻⁷	3.41	19927016	23679552
2.50 x 10 ⁻⁷	9.89 x 10 ⁻⁷	3.95	19166947	22919483
2.50 x 10 ⁻⁷	1.12 x 10 ⁻⁶	4.49	18045015	21797551
2.50 x 10 ⁻⁷	1.26 x 10 ⁻⁶	5.03	17292983	21045519
2.50 x 10 ⁻⁷	1.39 x 10 ⁻⁶	5.56	16274433	20026969
2.50 x 10 ⁻⁷	1.52 x 10 ⁻⁶	6.08	15612615	19365151
2.50 x 10 ⁻⁷	1.65 x 10 ⁻⁶	6.59	14779346	18531882
2.50 x 10 ⁻⁷	1.78 x 10 ⁻⁶	7.10	14215958	17968494
2.50 x 10 ⁻⁷	1.90 x 10 ⁻⁶	7.61	13551008	17303544
2.50 x 10 ⁻⁷	2.03 x 10 ⁻⁶	8.11	13316282	17068818
2.50 x 10 ⁻⁷	2.15 x 10 ⁻⁶	8.60	12594927	16347463
2.50 x 10 ⁻⁷	2.27 x 10 ⁻⁶	9.09	12164734	15917270
2.50 x 10 ⁻⁷	2.39 x 10 ⁻⁶	9.57	11707435	15459971
2.50 x 10 ⁻⁷	2.51 x 10 ⁻⁶	10.1	11368272	15120808
2.50 x 10 ⁻⁷	2.63 x 10 ⁻⁶	10.5	10946190	14698726

Polymer mixture **UT** vs. Con A (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 1 mM MnCl₂.



$$K_{\rm a} = 4.12 \text{ x } 10^5 \pm 6.32 \text{ x } 10^4 \text{ M}^{-1}$$

 $n = 1.0$

[ConA] / M	[TC-Con A] / M	[TC-Con A]/[ConA]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
2.50 x 10 ⁻⁷	0	0.00	25865657	0
2.50 x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.58	27741925	1876268
2.50 x 10 ⁻⁷	2.91 x 10 ⁻⁷	1.16	25206491	4411702
2.50 x 10 ⁻⁷	4.34 x 10 ⁻⁷	1.73	23997704	5620489
2.50 x 10 ⁻⁷	5.75 x 10 ⁻⁷	2.30	22686388	6931805
2.50 x 10 ⁻⁷	7.14 x 10 ⁻⁷	2.86	21075193	8543000
2.50 x 10 ⁻⁷	8.52 x 10 ⁻⁷	3.41	19927016	9691177
2.50 x 10 ⁻⁷	9.89 x 10 ⁻⁷	3.95	19166947	10451246
2.50 x 10 ⁻⁷	1.12 x 10 ⁻⁶	4.49	18045015	11573178
2.50 x 10 ⁻⁷	1.26 x 10 ⁻⁶	5.03	17292983	12325210
2.50 x 10 ⁻⁷	1.39 x 10 ⁻⁶	5.56	16274433	13343760
2.50 x 10 ⁻⁷	1.52 x 10 ⁻⁶	6.08	15612615	14005578
2.50 x 10 ⁻⁷	1.65 x 10 ⁻⁶	6.59	14779346	14838847
2.50 x 10 ⁻⁷	1.78 x 10 ⁻⁶	7.10	14215958	15402235
2.50 x 10 ⁻⁷	1.90 x 10 ⁻⁶	7.61	13551008	16067185
2.50 x 10 ⁻⁷	2.03 x 10 ⁻⁶	8.11	13316282	16301911
2.50 x 10 ⁻⁷	2.15 x 10 ⁻⁶	8.60	12594927	17023266
2.50 x 10 ⁻⁷	2.27 x 10 ⁻⁶	9.09	12164734	17453459
2.50 x 10 ⁻⁷	2.39 x 10 ⁻⁶	9.57	11707435	17910758
2.50 x 10 ⁻⁷	2.51 x 10 ⁻⁶	10.1	11368272	18249921
2.50 x 10 ⁻⁷	2.63 x 10 ⁻⁶	10.5	10946190	18672003

Polymer mixture **TC-Con A** vs. Con A (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 1 mM MnCl₂.





n = 1.0

[Con A] / M	[P-MAN]/M	[P-MAN]/[Con A]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
2.50 x 10 ⁻⁷	0	0.00	28177595	0
2.50 x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.58	25172183	3005412
2.50 x 10 ⁻⁷	2.91 x 10 ⁻⁷	1.16	23182137	4995458
2.50 x 10 ⁻⁷	4.34 x 10 ⁻⁷	1.73	22161347	6016248
2.50 x 10 ⁻⁷	5.75 x 10 ⁻⁷	2.30	20995697	7181898
2.50 x 10 ⁻⁷	7.14 x 10 ⁻⁷	2.86	20152325	8025270
2.50 x 10 ⁻⁷	8.52 x 10 ⁻⁷	3.41	19447501	8730094
2.50 x 10 ⁻⁷	9.89 x 10 ⁻⁷	3.95	18548054	9629541
2.50 x 10 ⁻⁷	1.12 x 10 ⁻⁶	4.49	17792521	10385074
2.50 x 10 ⁻⁷	1.26 x 10 ⁻⁶	5.03	16771163	11406432
2.50 x 10 ⁻⁷	1.39 x 10 ⁻⁶	5.56	16266602	11910993
2.50 x 10 ⁻⁷	1.52 x 10 ⁻⁶	6.08	15946274	12231321
2.50 x 10 ⁻⁷	1.65 x 10 ⁻⁶	6.59	15239444	12938151
2.50 x 10 ⁻⁷	1.78 x 10 ⁻⁶	7.10	14626894	13550701
2.50 x 10 ⁻⁷	1.90 x 10 ⁻⁶	7.61	14275403	13902192
2.50 x 10 ⁻⁷	2.03 x 10 ⁻⁶	8.11	13768572	14409023
2.50 x 10 ⁻⁷	2.15 x 10 ⁻⁶	8.60	13040006	15137589
2.50 x 10 ⁻⁷	2.27 x 10 ⁻⁶	9.09	12721860	15455735
2.50 x 10 ⁻⁷	2.39 x 10 ⁻⁶	9.57	12406105	15771490
2.50 x 10 ⁻⁷	2.51 x 10 ⁻⁶	10.1	12542365	15635230
2.50 x 10 ⁻⁷	2.63 x 10 ⁻⁶	10.5	11768778	16408817

Polymer mixture **P-MAN** vs. Con A (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 1 mM MnCl₂.



$$K_{\rm a} = 6.62 \text{ x } 10^5 \pm 4.65 \text{ x } 10^4 \text{ M}^{-1}$$

 $n = 1.0$

[ConA] / M	[P-GAL]/M	[P-GAL]/[ConA]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
2.50 x 10 ⁻⁷	0	0.00	32938272	0
2.50 x 10 ⁻⁷	1.46 x 10 ⁻⁷	0.58	31484386	1453886
2.50 x 10 ⁻⁷	2.91 x 10 ⁻⁷	1.16	29906964	3031308
2.50 x 10 ⁻⁷	4.34 x 10 ⁻⁷	1.73	28713769	4224503
2.50 x 10 ⁻⁷	5.75 x 10 ⁻⁷	2.30	27697396	5240876
2.50 x 10 ⁻⁷	7.14 x 10 ⁻⁷	2.86	26591746	6346526
2.50 x 10 ⁻⁷	8.52 x 10 ⁻⁷	3.41	25551507	7386765
2.50 x 10 ⁻⁷	9.89 x 10 ⁻⁷	3.95	24543387	8394885
2.50 x 10 ⁻⁷	1.12 x 10 ⁻⁶	4.49	23855686	9082586
2.50 x 10 ⁻⁷	1.39 x 10 ⁻⁶	5.56	22356097	10582175
2.50 x 10 ⁻⁷	1.52 x 10 ⁻⁶	6.08	21750643	11187629
2.50 x 10 ⁻⁷	1.65 x 10 ⁻⁶	6.59	21100385	11837887
2.50 x 10 ⁻⁷	1.78 x 10 ⁻⁶	7.10	20443336	12494936
2.50 x 10 ⁻⁷	1.90 x 10 ⁻⁶	7.61	19947746	12990526
2.50 x 10 ⁻⁷	2.03 x 10 ⁻⁶	8.11	19217792	13720480
2.50 x 10 ⁻⁷	2.15 x 10 ⁻⁶	8.60	18941431	13996841
2.50 x 10 ⁻⁷	2.27 x 10 ⁻⁶	9.09	18483481	14454791
2.50 x 10 ⁻⁷	2.39 x 10 ⁻⁶	9.57	18122559	14815713
2.50 x 10 ⁻⁷	2.51 x 10 ⁻⁶	10.1	17518840	15419432
2.50 x 10 ⁻⁷	2.63 x 10 ⁻⁶	10.5	17097473	15840799

Polymer mixture **P-GAL** vs. Con A (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 1 mM MnCl₂.



$$K_{\rm a} = 0.181 \pm 5.53 \text{ x } 10^3 \text{ M}^{-1}$$

n = 0.7

[LTB]/M	[T-LTB] / M	[T-LTB]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	22376250	0
5.00 x 10 ⁻⁷	6.16 x 10 ⁻⁸	0.12	20887323	1488927
5.00 x 10 ⁻⁷	1.23 x 10 ⁻⁷	0.25	20107991	2268259
5.00 x 10 ⁻⁷	1.84 x 10 ⁻⁷	0.37	19549935	2826315
5.00 x 10 ⁻⁷	2.45 x 10 ⁻⁷	0.49	19170234	3206016
5.00 x 10 ⁻⁷	3.67 x 10 ⁻⁷	0.73	18801540	3574710
5.00 x 10 ⁻⁷	4.28 x 10 ⁻⁷	0.86	18478697	3897553
5.00 x 10 ⁻⁷	4.88 x 10 ⁻⁷	0.98	18083211	4293039
5.00 x 10 ⁻⁷	5.49 x 10 ⁻⁷	1.10	17770624	4605626
5.00 x 10 ⁻⁷	6.09 x 10 ⁻⁷	1.22	17412119	4964131
5.00 x 10 ⁻⁷	6.69 x 10 ⁻⁷	1.34	17198652	5177598
5.00 x 10 ⁻⁷	7.29 x 10 ⁻⁷	1.46	16750315	5625935
5.00 x 10 ⁻⁷	7.89 x 10 ⁻⁷	1.58	16661624	5714626
5.00 x 10 ⁻⁷	8.48 x 10 ⁻⁷	1.70	16269541	6106709
5.00 x 10 ⁻⁷	9.08 x 10 ⁻⁷	1.82	16184774	6191476
5.00 x 10 ⁻⁷	9.67 x 10 ⁻⁷	1.93	15863954	6512296
5.00 x 10 ⁻⁷	1.03 x 10 ⁻⁶	2.05	15579532	6796718
5.00 x 10 ⁻⁷	1.09 x 10 ⁻⁶	2.17	15443595	6932655
5.00 x 10 ⁻⁷	1.14 x 10 ⁻⁶	2.29	15341979	7034271
5.00 x 10 ⁻⁷	1.20 x 10 ⁻⁶	2.41	15202089	7174161

Polymer mixture **T-LTB** vs. Con A (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 100 mM NaCl.



$$K_{\rm a} = 6.11 \text{ x } 10^6 \pm 9.38 \text{ x } 10^5 \text{ M}^{-1}$$

n = 1.0

[LTB]/M	[L1]/M	[UT]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	24635400	0
5.00 x 10 ⁻⁷	2.97 x 10 ⁻⁷	0.59	23561263	1074137
5.00 x 10 ⁻⁷	5.92 x 10 ⁻⁷	1.18	22800791	1834609
5.00 x 10 ⁻⁷	8.87 x 10 ⁻⁷	1.77	21988911	2646489
5.00 x 10 ⁻⁷	1.18 x 10 ⁻⁶	2.36	21352531	3282869
5.00 x 10 ⁻⁷	1.48 x 10 ⁻⁶	2.95	20561387	4074013
5.00 x 10 ⁻⁷	1.77 x 10 ⁻⁶	3.54	20277216	4358184
5.00 x 10 ⁻⁷	2.06 x 10 ⁻⁶	4.12	19769881	4865519
5.00 x 10 ⁻⁷	2.35 x 10 ⁻⁶	4.70	19313969	5321431
5.00 x 10 ⁻⁷	2.64 x 10 ⁻⁶	5.28	19049536	5585864
5.00 x 10 ⁻⁷	2.93 x 10 ⁻⁶	5.86	18520105	6115295
5.00 x 10 ⁻⁷	3.22 x 10 ⁻⁶	6.44	18306609	6328791
5.00 x 10 ⁻⁷	3.51 x 10 ⁻⁶	7.02	17997043	6638357
5.00 x 10 ⁻⁷	3.80 x 10 ⁻⁶	7.60	17371509	7263891
5.00 x 10 ⁻⁷	4.08 x 10 ⁻⁶	8.17	17091921	7543479
5.00 x 10 ⁻⁷	4.37 x 10 ⁻⁶	8.74	16764718	7870682
5.00 x 10 ⁻⁷	4.66 x 10 ⁻⁶	9.31	16212818	8422582
5.00 x 10 ⁻⁷	4.94 x 10 ⁻⁶	9.88	15937195	8698205
5.00 x 10 ⁻⁷	5.23 x 10 ⁻⁶	10.5	15789456	8845944
5.00 x 10 ⁻⁷	5.51 x 10 ⁻⁶	11.0	15443819	9191581
5.00 x 10 ⁻⁷	5.79 x 10 ⁻⁶	11.6	15046132	9589268

Polymer mixture **UT** vs. LTB (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 100 mM NaCl.



$$K_{\rm a} = 1.64 \text{ x } 10^5 \pm 1.32 \text{ x } 10^4 \text{ M}^{-1}$$

n = 0.8

[LTB] / M	[TC-LTB]/M	[TC-LTB]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	25234446	0
5.00 x 10 ⁻⁷	2.97 x 10 ⁻⁷	0.59	23518662	1715784
5.00 x 10 ⁻⁷	5.92 x 10 ⁻⁷	1.18	22382614	2851832
5.00 x 10 ⁻⁷	8.87 x 10 ⁻⁷	1.77	22106351	3128095
5.00 x 10 ⁻⁷	1.18 x 10 ⁻⁶	2.36	20912294	4322152
5.00 x 10 ⁻⁷	1.48 x 10 ⁻⁶	2.95	19783649	5450797
5.00 x 10 ⁻⁷	1.77 x 10 ⁻⁶	3.54	19499317	5735129
5.00 x 10 ⁻⁷	2.06 x 10 ⁻⁶	4.12	18572947	6661499
5.00 x 10 ⁻⁷	2.35 x 10 ⁻⁶	4.70	17845253	7389193
5.00 x 10 ⁻⁷	2.64 x 10 ⁻⁶	5.28	17238958	7995488
5.00 x 10 ⁻⁷	2.93 x 10 ⁻⁶	5.86	16287585	8946861
5.00 x 10 ⁻⁷	3.22 x 10 ⁻⁶	6.44	15819056	9415390
5.00 x 10 ⁻⁷	3.51 x 10 ⁻⁶	7.02	14852250	10382196
5.00 x 10 ⁻⁷	3.80 x 10 ⁻⁶	7.60	14190464	11043982
5.00 x 10 ⁻⁷	4.08 x 10 ⁻⁶	8.17	13892458	11341988
5.00 x 10 ⁻⁷	4.37 x 10 ⁻⁶	8.74	13272074	11962372
5.00 x 10 ⁻⁷	4.66 x 10 ⁻⁶	9.31	13113063	12121383
5.00 x 10 ⁻⁷	4.94 x 10 ⁻⁶	9.88	12473677	12760769
5.00 x 10 ⁻⁷	5.23 x 10 ⁻⁶	10.5	12052792	13181654
5.00 x 10 ⁻⁷	5.51 x 10 ⁻⁶	11.0	11542210	13692236
5.00 x 10 ⁻⁷	5.79 x 10 ⁻⁶	11.6	11146696	14087750

Polymer mixture **TC-LTB** vs. LTB (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 100 mM NaCl.





$$K_{\rm a} = 1.76 \text{ x } 10^5 \pm 1.24 \text{ x } 10^4 \text{ M}^{-1}$$

n = 1.0

[LTB] / M	[P-MAN] / M	[P-MAN]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	22499222	0
5.00 x 10 ⁻⁷	2.97 x 10 ⁻⁷	0.59	22018864	480358
5.00 x 10 ⁻⁷	5.92 x 10 ⁻⁷	1.18	21166598	1332624
5.00 x 10 ⁻⁷	8.87 x 10 ⁻⁷	1.77	20785448	1713774
5.00 x 10 ⁻⁷	1.18 x 10 ⁻⁶	2.36	20291807	2207415
5.00 x 10 ⁻⁷	1.48 x 10 ⁻⁶	2.95	20004456	2494766
5.00 x 10 ⁻⁷	1.77 x 10 ⁻⁶	3.54	19717017	2782205
5.00 x 10 ⁻⁷	2.06 x 10 ⁻⁶	4.12	19446339	3052883
5.00 x 10 ⁻⁷	2.35 x 10 ⁻⁶	4.70	18941646	3557576
5.00 x 10 ⁻⁷	2.64 x 10 ⁻⁶	5.28	18384582	4114640
5.00 x 10 ⁻⁷	2.93 x 10 ⁻⁶	5.86	18277050	4222172
5.00 x 10 ⁻⁷	3.22 x 10 ⁻⁶	6.44	17968609	4530613
5.00 x 10 ⁻⁷	3.51 x 10 ⁻⁶	7.02	17700953	4798269
5.00 x 10 ⁻⁷	3.80 x 10 ⁻⁶	7.60	17289307	5209915
5.00 x 10 ⁻⁷	4.08 x 10 ⁻⁶	8.17	16894996	5604226
5.00 x 10 ⁻⁷	4.37 x 10 ⁻⁶	8.74	16550796	5948426
5.00 x 10 ⁻⁷	4.66 x 10 ⁻⁶	9.31	15916641	6582581
5.00 x 10 ⁻⁷	4.94 x 10 ⁻⁶	9.88	15619212	6880010
5.00 x 10 ⁻⁷	5.23 x 10 ⁻⁶	10.5	15423000	7076222
5.00 x 10 ⁻⁷	5.51 x 10 ⁻⁶	11.0	15241631	7257591
5.00 x 10 ⁻⁷	5.79 x 10 ⁻⁶	11.6	14835424	7663798

Polymer mixture **P-MAN** vs. LTB (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 100 mM NaCl.



$$K_{\rm a} = 0.625 \pm 4.27 \ {\rm x} \ 10^4 \ {\rm M}^{-1}$$

n = 1.0

[LTB]/M	[P-GAL] / M	[P-GAL]/[LTB]	Fluorescence Intensity / c.p.s.	ΔI / c.p.s.
5.00 x 10 ⁻⁷	0	0.00	22173180	0
5.00 x 10 ⁻⁷	2.97 x 10 ⁻⁷	0.59	21559760	613420
5.00 x 10 ⁻⁷	5.92 x 10 ⁻⁷	1.18	20991129	1182051
5.00 x 10 ⁻⁷	8.87 x 10 ⁻⁷	1.77	20004150	2169030
5.00 x 10 ⁻⁷	1.18 x 10 ⁻⁶	2.36	19488917	2684263
5.00 x 10 ⁻⁷	1.48 x 10 ⁻⁶	2.95	18382626	3790554
5.00 x 10 ⁻⁷	1.77 x 10 ⁻⁶	3.54	17472041	4701139
5.00 x 10 ⁻⁷	2.06 x 10 ⁻⁶	4.12	16437427	5735753
5.00 x 10 ⁻⁷	2.35 x 10 ⁻⁶	4.70	16222599	5950581
5.00 x 10 ⁻⁷	2.64 x 10 ⁻⁶	5.28	15778687	6394493
5.00 x 10 ⁻⁷	2.93 x 10 ⁻⁶	5.86	15089178	7084002
5.00 x 10 ⁻⁷	3.22 x 10 ⁻⁶	6.44	14521280	7651900
5.00 x 10 ⁻⁷	3.51 x 10 ⁻⁶	7.02	14274805	7898375
5.00 x 10 ⁻⁷	3.80 x 10 ⁻⁶	7.60	13822607	8350573
5.00 x 10 ⁻⁷	4.08 x 10 ⁻⁶	8.17	13293536	8879644
5.00 x 10 ⁻⁷	4.37 x 10 ⁻⁶	8.74	12823964	9349216
5.00 x 10 ⁻⁷	4.66 x 10 ⁻⁶	9.31	12534525	9638655
5.00 x 10 ⁻⁷	4.94 x 10 ⁻⁶	9.88	12087849	10085331
$5.00 \ge 10^{-7}$	5.23 x 10 ⁻⁶	10.5	11538792	10634388
5.00 x 10 ⁻⁷	5.51 x 10 ⁻⁶	11.0	11375055	10798125
5.00 x 10 ⁻⁷	5.79 x 10 ⁻⁶	11.6	10980085	11193095

Polymer mixture **P-GAL** vs. LTB (c.p.s.: counts per second). 100 mM HEPES, pH 7.1, 1 mM CaCl₂, 100 mM NaCl.



$$K_{\rm a} = 2.45 \text{ x } 10^5 \pm 9.83 \text{ x } 10^3 \text{ M}^{-1}$$

 $n = 0.7$













References

- 1. W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, 4th edn., 1996.
- 2. I. T. Crosby, G. A. Pietersz and J. A. Ripper, Aust. J. Chem., 2008, 61, 138-143.
- 3. A. W. Jackson and D. A. Fulton, *Chem. Commun.*, 2011, 47, 6807-6809.
- 4. A. W. Jackson and D. A. Fulton, *Macromolecules*, 2009, 43, 1069-1075.
- 5. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, 35, 6754-6756.
- 6. K. Bock, I. Lundt and C. Pedersen, *Tetrahedron Lett.*, 1973, 14, 1037-1040.
- Z. Han, J. S. Pinkner, B. Ford, R. Obermann, W. Nolan, S. A. Wildman, D. Hobbs, T. Ellenberger, C. K. Cusumano, S. J. Hultgren and J. W. Janetka, *J. Med. Chem.*, 2010, 53, 4779-4792.
- 8. Bryan Klekota, Mark H. Hammond and B. L. Miller, *Tetrahedron Lett.*, 1997, 38, 8639–8642.