# Supporting information

# Quantitative Analysis of Interactions between Mannose-containing Glycopolymers

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## 1. Material

*D*-Mannose, triethyl amine (TEA) (99%), 2,2'-azobis (isobutyronitrile) (AIBN) (98%), calcium chloride (95%), 2-[4-(2-Hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) (99%), 4,4"-azobis(4-cyanovaleric acid) (V-501) (98.0%), carbon disulfide (98.0%), toluene (99.5%), *N,N'*-dicyclohexylcarbodiimide (DCC) (95.0%), 4-dimethylaminopyridine (DMAP) (99.0%), ethanol (99.5%), silver chloride (99.5%), 1,8-diazabicyclo[5,4,0]undec-7-ene (97%), trimethylchlorosilane (98%) and deuterium oxide ($D_2O$, 99.8%) were purchased from Wako. *N*,*N*-diisopropylethlamine (99%), iodine (98.0%), 1-butane thiol (97.0%), sodium hydride (60%, dispersion in paraffin liquid), methacryloyl chloride (80%), Osmium Tetroxide (4% in Water), *N,N*-Diisopropylethylamine (99%) and poly(ethylene glycol)monomethyl ether (Mw: 4000) were purchased from Tokyo Chemical Industry. Sodium azide (97%), sodium chloride (99%), magnesium chloride hexahydrate (99%), potassium chloride (99.5%), dry dichloromethane (99.5%), dry *N,N*-dimethylformamide (DMF) (99.5%), ethyl acetate (99.3%), *D*(+)-glucose (98.0%), sodium thiosulfate pentahydrate (99.0%) and diethyl ether (99.0%), hexane (95%) and acetone (99%) and ethyl acetate (99%) were purchased from Kanto Chemical. 2-chloro-1,3-dimethylimidazolium chloride, copper (I) bromide (97.0%) were purchased from Aldrich. Dimethyl sulfoxide (DMSO, 98%) was purchased from Kishida. Propargyl alcohol (99%) and cupper bromide (I) (99.99%) was purchased from sigma Aldrich. *D*(+)-galactose (99+%) were purchased from ACROS ORGANICS.

## 2. Characterization

### $^1$H NMR analysis

$^1$H NMR spectra were recorded on a JNM-ECZ400 spectrometer (JEOL, Tokyo, Japan) using $CDCl_3$, $d_6$-DMSO, $d_6$-acetone or $D_2O$ as a solvent.

### Mass spectrometer

Each sample was dissolved in methanol. Mass spectrometer was performed by ACQUITY UPLC H-Class PLUS System (Sample Manager FTN-H, Quaternary Solvent Manager, Column Manager and PDA eλ Detector) and ACQUITY QDa.

### Gel permeation chromatography (GPC) analysis

Gel permeation chromatography (GPC) with organic solvent was performed on a HLC-8320 GPC Eco-SEC system equipped with a TSKgel Super AW guard column and TSKgel Super AW (4000, 3000 and 2500) columns (Tosoh, Tokyo Japan). GPC analyses were performed by injecting 20 μL of a polymer solution (1 g $L^{-1}$) in DMF buffer containing 10 mM LiBr. The buffer solution was also used as the eluent at a flow rate of 0.5 mL $min^{-1}$. The GPC system was calibrated using a poly(methyl methacrylate) standard (Shodex).

**QCM measurement**

A 27 MHz quartz crystal microbalance (QCM) system (Affnix Q8, Ulvac Inc., Japan) was used to monitor the interaction. 200 μL of 1 wt% SDS aqueous solution was added to the QCM cell and the gold surface was rubbed with a cotton swab. The QCM cell with SDS solution was incubated for 10 mins. Each cell was washed 10 times with Milli-Q and the Milli-Q was removed from the surface using $N_2$ blow. Piranha solution (4 μL) was dropped onto the gold surface, left for 10 mins and washed with Milli-Q (three cycle). In the last cycle, the gold surface was replaced with Milli-Q 10 times to prevent it from coming into contact with air. The QCM cell was placed in the QCM apparatus and monitored with 100 μL of Milli-Q until the frequency was constant. Once the frequency was constant, 100 μL of each glycopolymer (**pMan$_{200}$**, **pGal$_{200}$** and **pGlc$_{200}$**) was added to bring the concentration in the cell to 10 g/L, and the cell was kept at 15ºC for 2 hours. To remove unfixed glycopolymer from the cell, the cell was washed with Milli-Q three times and then washed again with HEPES buffer and monitored until the frequency became constant. After the frequency became constant, each PEG-terminated glycopolymer (**P$_{90}$Man$_{200}$**, **P$_{90}$Gal$_{200}$** and **P$_{90}$Glc$_{200}$**) or PEG solution was added successively at 15ºC, and the cell was measured until the frequency became constant.

**X-ray photoelectron spectroscopy (XPS) measurement**

XPS measurement was performed on a Shimadzu/Kratos AXIS-ultra (Kratos Analytical Ltd., Manchester, UK, Shimadzu Co., Kyoto, Japan) for the analysis of the glycopolymer immobilized. All XPS spectra energy referenced to the C (1s) photoemission peak at 285.0 eV. The substrates for XPS measurements were prepared by incubate aqueous solution (10 g/L) of **pMan$_{200}$**, **pGal$_{200}$** and **pGlc$_{200}$** for 2 h on LaSFN9 glass substrates coated Au (50 nm).

**Turbidity measurement by UV-Vis spectrometer**

Each glycopolymer (**pMan$_{200}$**, **pGal$_{200}$** and **pGlc$_{200}$**) were dissolved in HEPES buffer (HEPES: 10 mM, NaCl: 137 mM, KCl: 2.7 mM, $CaCl_2$: 1.8 mM) at 1 g $L^{-1}$. After incubation at 15 ºC for 48 h, the absorbance of 600 nm was recorded.

**Dynamic light scattering (DLS) measurement**

Each PEG-terminated glycopolymer (**P$_{90}$Man$_{200}$**, **P$_{90}$Gal$_{200}$** and **P$_{90}$Glc$_{200}$**) were dissolved in HEPES buffer (HEPES: 10 mM, NaCl: 137 mM, KCl: 2.7 mM, $CaCl_2$: 1.8 mM) at 1 g $L^{-1}$. Each DHBG aqueous solution was shaken at 40ºC for 10 mins. Then, each solution was incubated at 5 ºC for 20 h. After incubation, DLS measurement was carried out at 5 ºC.

**Transmission electron microscope (TEM) observation**

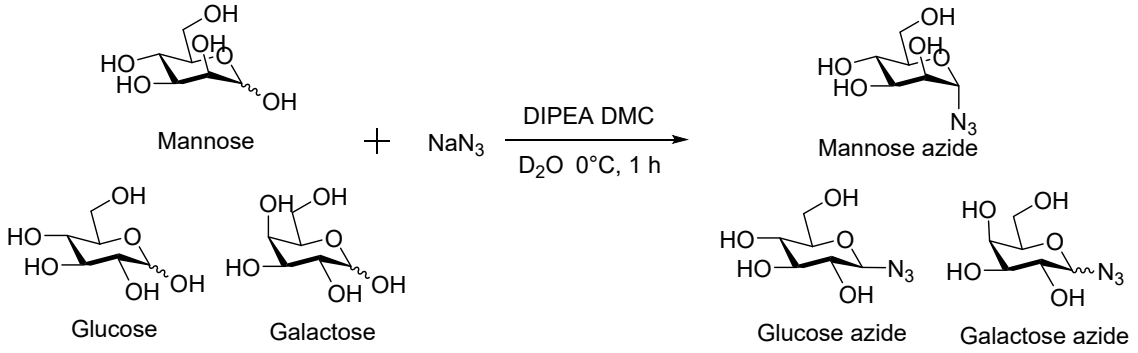
TEM observation of each DHBG was performed using an FEI TECNAI-20 system (Thermo). The TEM grid was hydrophilized by plasma treatment for 30 s and then 2 μL of each polymer solution was dropped onto the grid. The grid was incubated for 1 min at 5 ºC, excess solution was removed with

paper, and then uranyl acetate solution was dropped onto the TEM grid and incubated for 30 s at 5 ºC. Excess solution was again removed with paper and then TEM observation was conducted at 120 kV. The polymer was dissolved in HEPES buffer (HEPES, 10 mM; NaCl, 136.9 mM; KCl, 2.68 mM; $CaCl_2$, 1.80 mM).

## 3. Experimental

### 3.6 3.1 Synthesis of sugar azide

### Scheme.3- 1 Azidation of sugar.




Mannose, galactose and glucose were used for this article. Sugar (7.9 mmol), $NaN_3$ (78.9 mmol), *N,N*-Diisopropylethylamine (71 mmol) were dissolve in $D_2O$ (31.2 mL) with stirring in ice bath. After the mixture had cooled sufficiently, 2-chloro-1,3-dimethylimidazolium chloride (DMC) (23.7 mmol) were added into the mixture. Then the mixture was stirred for 1 h at 0°C. The progress of reaction was confirmed by $^1$H NMR. After concentration of the reaction mixture and addition of ethanol, the solid was removed by filtration. The filtrate was concentrated *in vacuo* and the product was dissolved in water. The product was ion changed by the addition of 1N NaOH aq to convert the impurity DIPEA hydrochloride to DIPEA. Then the mixture was washed using dichloromethane and the aqueous phase was concentrated *in vacuo*. The product was concentrated and addition ethanol, the solid was removed by filtration. The filtrate was concentrated and freeze dried to give yellow solid. These products were confirmed by $^1$H NMR (Fig.S4-1 to S4-3) and mass spectroscopy. (Crude yield; mannose azide 110.1%, galactose azide 118.0% and glucose azide 120.0%)

sugar azide was yellow in color. it is considered that this yellow color to be due to the Cl of DMC. As a result, the yield exceeded 100%. On the other hand, in the subsequent Huisgen reaction, azide reacts specifically with alkynes and was used without further purification.

Mannose azide

$^1$H NMR (400 MHz, $D_2O$), δ (ppm): 5.44 (d, J=1.6 Hz, –C**H**-$N_3$), 3.77 (d, J=10.1 Hz, -C**H**$_2$-OH), 3.73 (dd, J=2.3, 3.2 Hz, -C**H**$_2$-OH, 2H), 3.65 (t, J=6.4 Hz, -CH-C**H**-$CH_2$-, 1H), 3.60 (s, -C**H**-CH-

CH-$N_3$, 1H), 3.52 (dd, J=4.1, 9.6 Hz, -CH-C**H**-$CH_2$, 1H), 3.49 (t, J=5.3 Hz, -CH-C**H**-CH-$N_3$, 1H).
ESI-TOF-Ms (positive mode): 228.16 (+$Na^+$)

Galactose azide

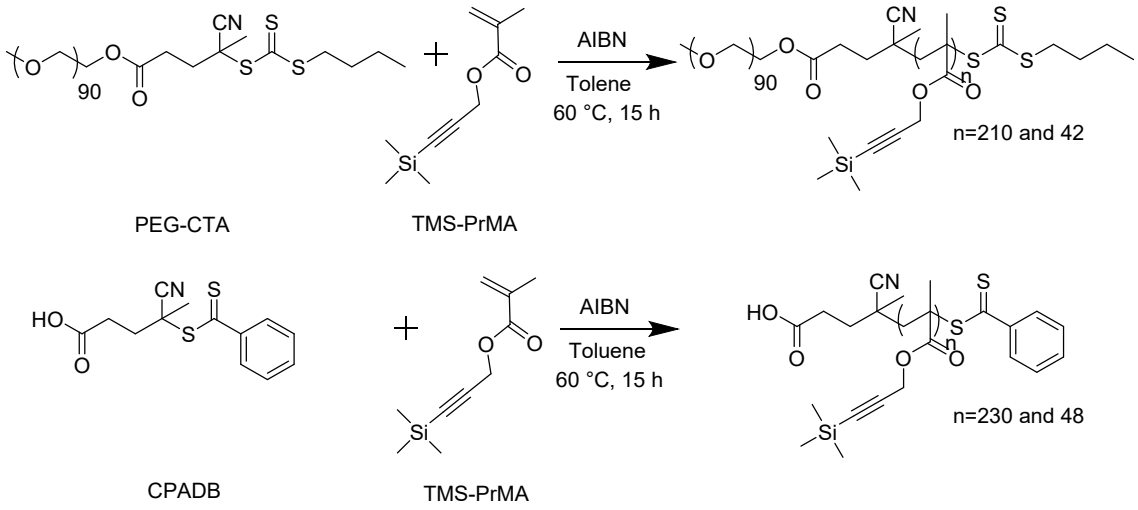
$^1$H NMR (400 MHz, $D_2O$), δ (ppm): 5.56 (d, J=4.0 Hz, –C**H**-$N_3$), 4.67 (d, J=8.4 Hz, –C**H**-$N_3$), 3.4-4.1 (galactose, galactose azide and ethanol)
ESI-TOF-Ms (positive mode): 228.16 (+$Na^+$)

Glucose azide

$^1$H NMR (400 MHz, $D_2O$), δ (ppm): 4.75 (d, J=8.4 Hz, –C**H**-$N_3$), 3.90 (dd, J=2.4 Hz, 12.8 Hz -C**H**$_2$-OH, 1H), 3.72 (dd, J=5.6, 12.4 Hz, -C**H**$_2$-OH, 1H), 3.65 (m, J=8.8, 3.2, 6.0 Hz, -CH-C**H**-$CH_2$-, 1H), 3.39-3.52 (t, J=9.6, 9.2 Hz, -C**H**-CH-CH-$N_3$, 1H and -CH-C**H**-$CH_2$, 1H), 3.24 (t, J=8.8 Hz, -CH-C**H**-CH-$N_3$, 1H).
ESI-TOF-Ms (positive mode): 250.8 (+formic acid)

## 3.7 3.2. General procedure for RAFT polymerization

**Scheme.3- 2 General procedure for RAFT polymerization.**




The synthesis of 3-(trimethylsilyl)prop-2-yn-1-yl methacrylate (TMS-PrMA) and poly (ethylene glycol) 4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoate (PEG-CTA) are described in Chapter 2 and 3, respectively. The polymer backbone were TMS-PrMA was introduced into a glass tube and mixed with a toluene solution of PEG-CTA or CPADB as the RAFT agent and AIBN as the radical initiator. The feed ratio of TMS-PrMA and RAFT agent, AIBN are shown in Table.1. The tube was degassed with freeze–pump–thaw cycles (three times), sealed under vacuum, and transferred to an oil

bath at 60 °C. After heating for 15 h, polymerization was stopped by exposing the solution to the air. The monomer conversion was calculated from $^1$H NMR, which were 76.0 (**P90TMS200**), 81.4% and (**TMS200**). The reaction solution was dialyzed against acetone and concentrated in *vacuo* to remove monomer. In the case of **P90TMS200**, the polymer was precipitated in $CHCl_3$ / Hexane mixture (Hex : $CHCl_3$ = 13 : 1) to remove inactive PEG and the supernatant was collected by centrifugation. The supernatant liquid was concentrated *in vacuo* to get the product. The degree of polymerizations were determined by $^1$H NMR (Fig.S4-4, S4-6, S4-8 and S4-10), which were 210 (**P90TMS200**) and 230 (**TMS200**), respectively. The polydispersity and $M_n$ of the polymer was determined by GPC, which were 1.23 and 37000 (**P90TMS200**) and 1.23 and 31700 (**TMS200**) (Fig.S5-1 to S5-3).

**Table.1 The feed ratio of raft polymerization.**

| | TMS-PrMA | RAFT agent | AIBN | Toluene |
|---|---|---|---|---|
| P90TMS200 | 5.00 mmol | $4.35 \times 10^{-2}$ mmol | $8.70 \times 10^{-3}$ mmol | 2.50 mL |
| TMS200 | 4.52 mmol | $2.30 \times 10^{-2}$ mmol | $4.52 \times 10^{-3}$ mmol | 1.13 mL |

**P90TMS200**

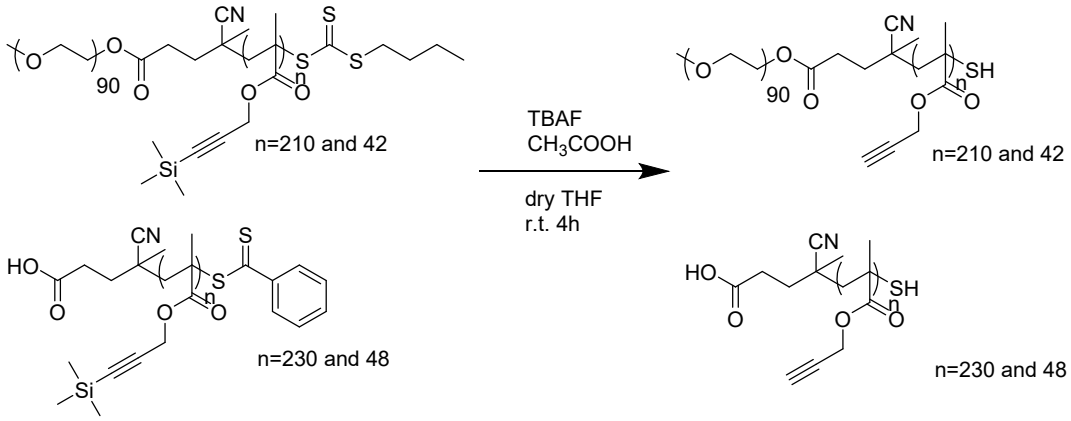
$^1$H NMR (400 MHz, $CDCl_3$), δ (ppm): 4.60 (s, -C**H**$_2$-C≡C), 3.65 (s, -(C**H**$_2$-C**H**$_2$-O)$_{90}$-), 3.38 (s, -CH$_2$-CH$_2$-O-C**H**$_3$), 1.85-1.94 (brdd, -C(CH$_3$)-C**H**$_2$-), 0.92-1.09 (-C(C**H**$_3$)-CH$_2$-), 0.20 (s, -Si-(C**H**$_3$)$_3$).

**TMS200**

$^1$H NMR (400 MHz,Acetone-d6), δ (ppm): 8.11 (brs, -CH-CH-C-), 7.72 (brs, -CH-CH-CH-C-), 7.55 (brs, -CH-CH-C-), 4.72 (brs, -C**H$_2$**- C≡C-, 2H), 1.92-2.02 (brs, -C**H$_2$**-C-CH$_3$, 2H), 1.01-1.16 (brs, -CH$_2$-C-C**H$_3$**, 3H), 0.24 (brs, Si(CH3)3, 9H).

### 3.8 3.3 Deprotection TMS group in the polymer

**Scheme.3- 3 Deprotection TMS group in the polymer.**




The polymer (1 equiv. of TMS groups in polymer backbone) was dissolved in dry THF ( molar concentration of TMS groups, 0.05M) with TBAF (1.5 equiv. ) and acetic acid (1.5 equiv.) in Teflon flask. The mixture was stirred for 4 h at room temperature. The mixture solution was purified by dialysis against acetone. The resultant polymer solution was concentrated *in vacuo*. The deprotection rate of TMS group was confirmed by $^1$H NMR, which were over 99.0% (Fig.S4-5, S4-7, S4-9 and S4-11).

**<u>P90Pr200 and P90Pr50</u>**

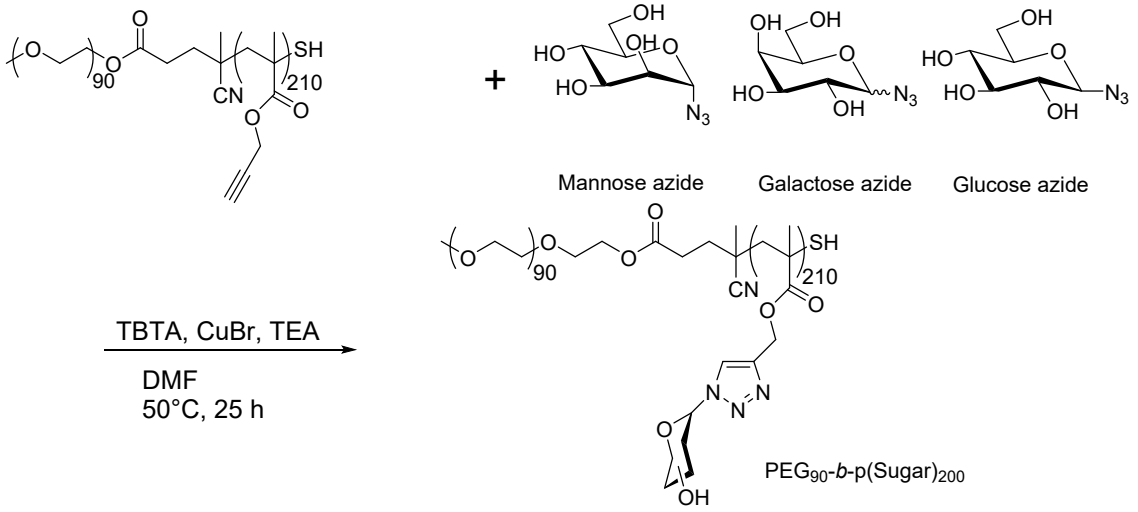
$^1$H NMR (400 MHz, $CDCl_3$), δ (ppm): 4.62 (s, -C**H**$_2$-C≡C), 3.64 (s, -(C**H**$_2$-C**H**$_2$-O)$_{90}$-), 3.38 (s, -$CH_2$-$CH_2$-O-C**H**$_3$), 2.51 (s, - C≡C**H**, 1H), 1.64-1.89 (brdd, -C($CH_3$)-C**H**$_2$-), 0.94-1.09 (-C(C**H**$_3$)-$CH_2$-)

**<u>Pr200 and Pr50</u>**

$^1$H NMR (400 MHz,$CDCl_3$), δ (ppm): 4.62 (brs, -C**H$_2$**- C≡C-, 2H), 2.51 (s, - C≡C**H**, 1H), 1.62-1.90 (brs, -C-C**H$_2$**-C-, 2H) , 0.94-1.09 (brs, -$CH_2$-C-C**H$_3$**, 3H)

### 3.9 3.4 Huisgen reaction for P90Pr200 or Pr200 and Sugar azide

**Scheme.3- 4 Synthesis of DHBG via Huisgen reaction.**

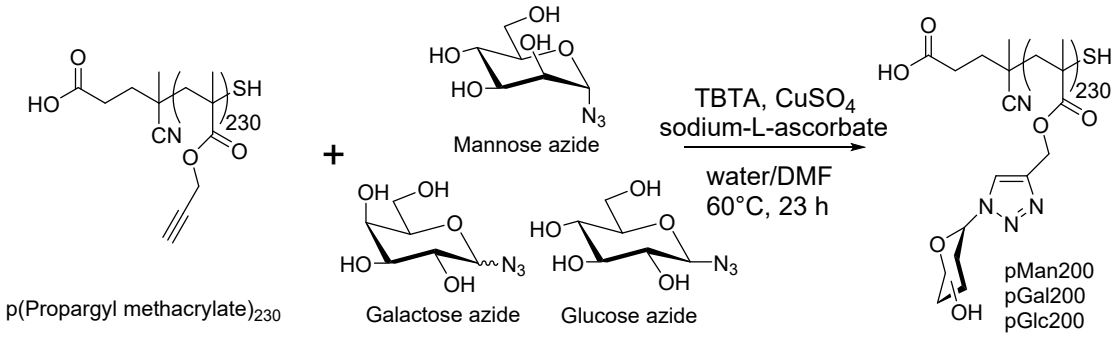



P90Pr200 (1 equiv. of alkyne group in polymer backbone), sugar azide (mannose azide, galactose azide and glucose azide) (5 equiv.) and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (0.25 equiv.) was dissolved in DMF (the molar concentration of alkyne; 0.07M). The reaction mixture were degassed by $N_2$ bubbling for 10 mins. Then CuBr (0.25 equiv.) and TEA (0.25 equiv.) was added in the reaction mixture and degassed again for 10 mins. The reaction mixture was stirred for 25 h at 50ºC under a nitrogen atmosphere. The mixture was then dialyzed against DMSO for 24 h, Milli-Q (pH = 4) for 24 h, and Milli-Q (pH=7) for 24 h. The final solution was freeze-dried to obtain the DHBG (yield: 25% for $\mathbf{P_{90}Man_{200}}$, 37% for $\mathbf{P_{90}Gal_{200}}$ and 30% for $\mathbf{P_{90}Glc_{200}}$; These low yield is because the initial polymer weight is shifted by the solvent that could not be fully removed from the polymer.). The sugar incorporation ratio was confirmed by $^1$H NMR, which were over 99.0% for all polymer (Fig.S4-8).

$^1$H NMR (400 MHz, d6-DMSO), $\delta$ (ppm): 8.30-8.40 (triazole), 5.6-6.0 (anomer of sugar) 3.51 (s, -(C**H**$_2$-C**H**$_2$-O)$_{90}$-), 0.50–2.00 (-C(C**H**$_3$)-C**H**$_2$- and -C(CH$_3$)-C**H**$_2$-).

## 3.10 3.5 Huisgen reaction for Pr200 and sugar azide

**Scheme.3- 5 Synthesis of glycopolymer via Huisgen reaction.**




Homopolymer with sugar moiety were synthesized following scheme 4. Pr230 (1 equiv. of alkyne group in polymer backbone), sugar azide (5 equiv.) and TBTA (0.4 equiv.) were dissolved in DMF. Sodium-L-ascorbate (2 equiv.) and $CuSo_4$ (0.4 equiv.) were dissolved in water, respectively. Then, each aqueous solution was added into the reaction solution. The final alkyne concentration was 0.07 M and the ratio of the solvent was DMF : Water = 3 : 1. The reaction solution was stirred for 23 h at 60ºC with $N_2$ bubbling. The mixture was then dialyzed against DMSO for 24 h, Milli-Q (pH = 4) for 24 h, and Milli-Q (pH=7) for 24 h. The final solution was freeze-dried to obtain the DHBG (yield: 51% for **pMan$_{200}$**, 68% for **pGal$_{200}$** and 69% for **pGlc$_{200}$**. The sugar incorporation ratio was confirmed by $^1$H NMR, which were over 99.0% for all polymer (Fig.S4-9).

$^1$H NMR (400 MHz, d6-DMSO), $\delta$ (ppm): 8.30-8.40 (triazole), 5.6-6.0 (anomer of sugar), 0.50–2.00 (-C(C**H**$_3$)-C**H**$_2$- and -C(CH$_3$)-C**H**$_2$-).

## 4. NMR spectrum

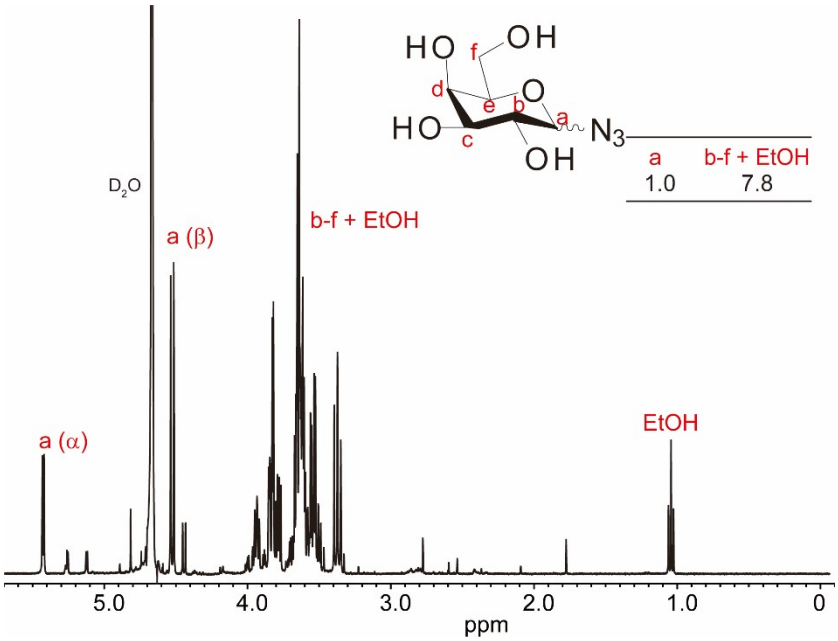



**Figure.S4- 1 $^{1}$H NMR of galactose azide. α-Galactose azide and β-glucose azide was obtained.**

**The anomer ratio is about α:b=1:9.**

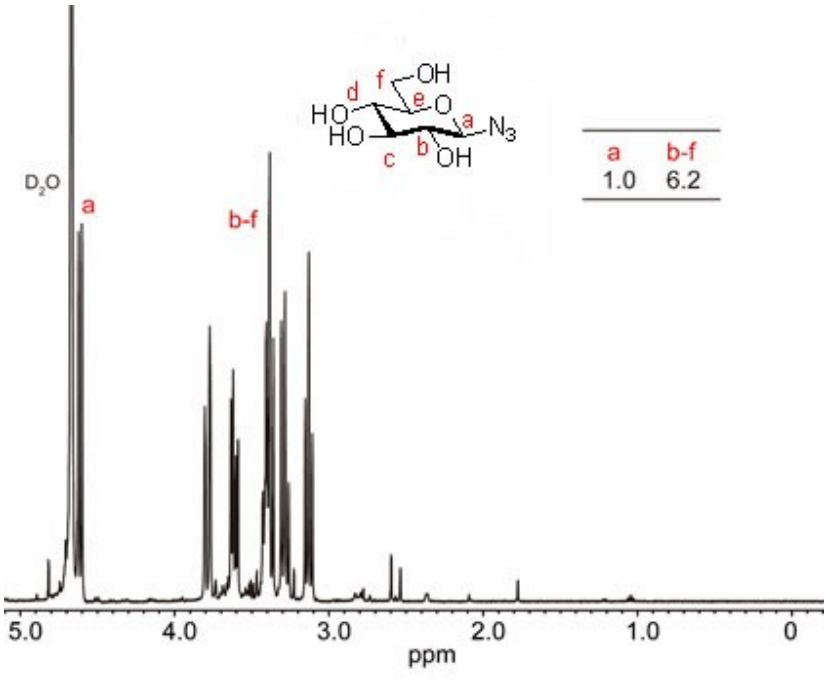



**Figure.S4- 2 $^{1}$H NMR of glucose azide. β-Glucose azide was observed.**

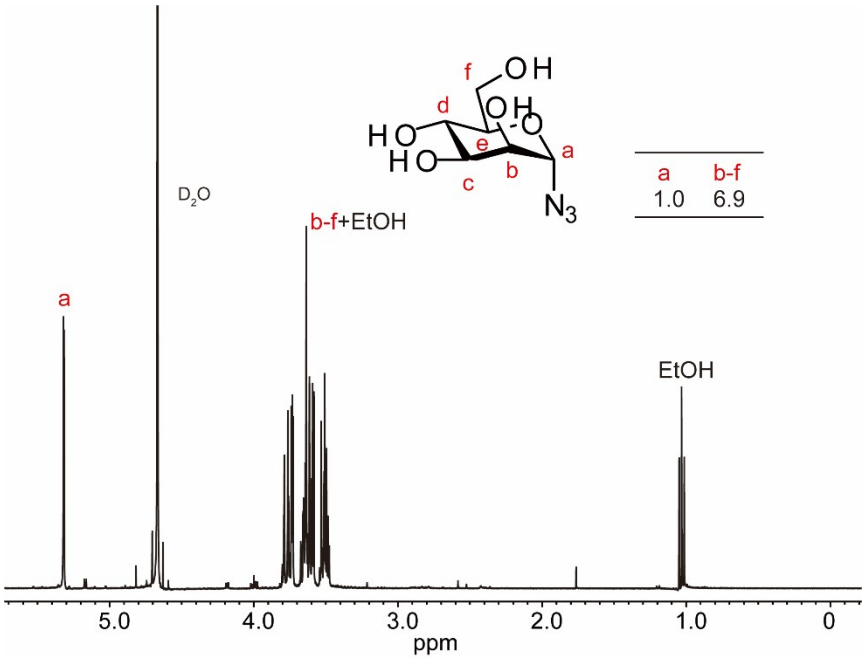



**Figure.S4- 3 $^{1}$H NMR of mannose azide. Only α-mannose azide was obtained. (*Polymer Chemistry*, 2011, *2*(1), 107-113.)**

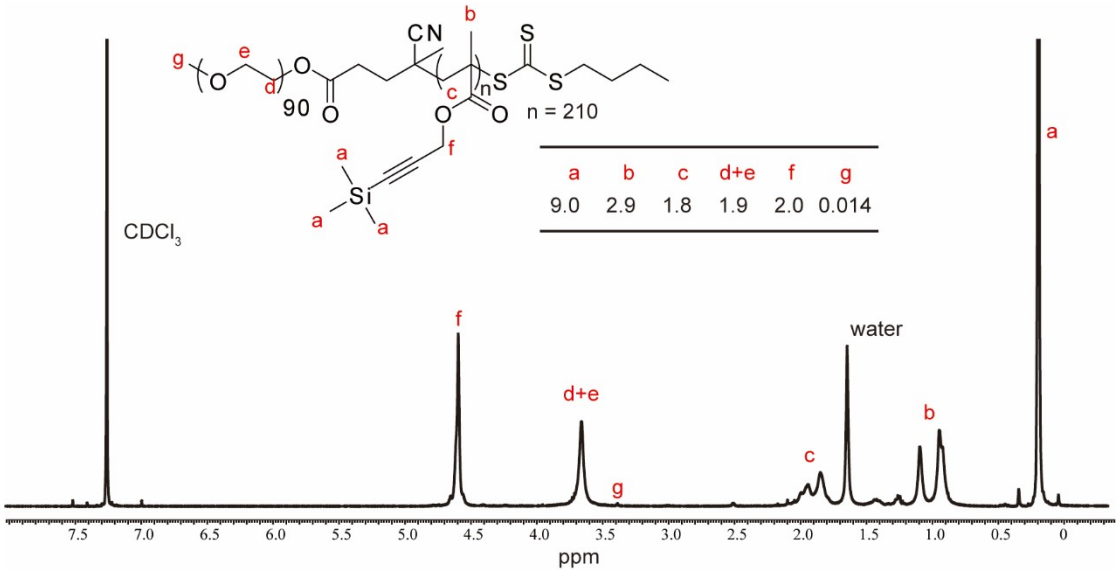



**Figure.S4- 4 $^{1}$H NMR of P90TMS200.**

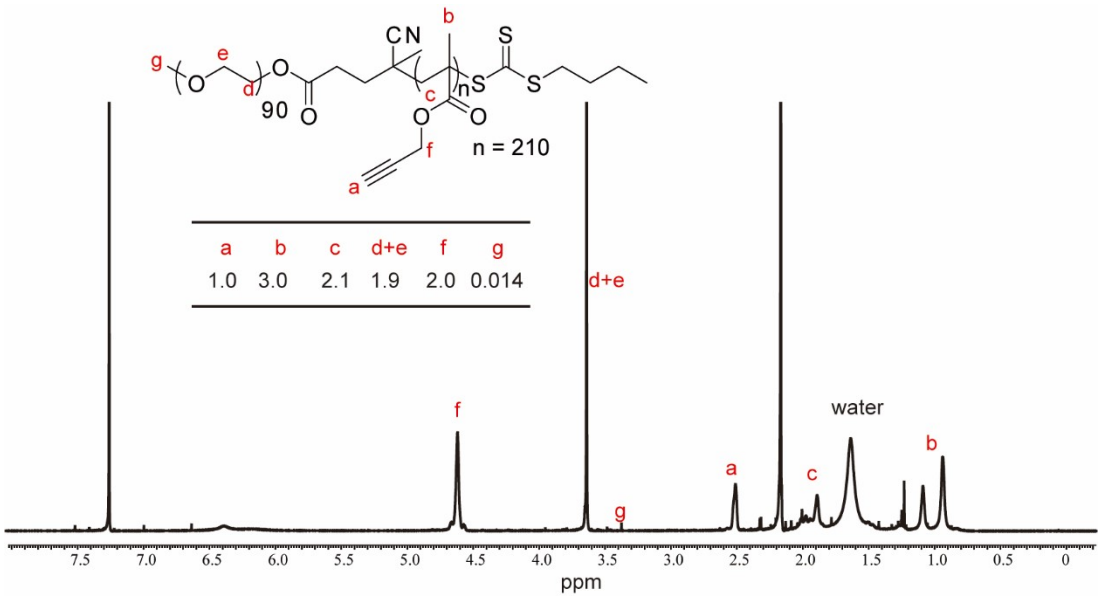



**Figure.S4- 5 $^{1}$H NMR of P90Pr200.**

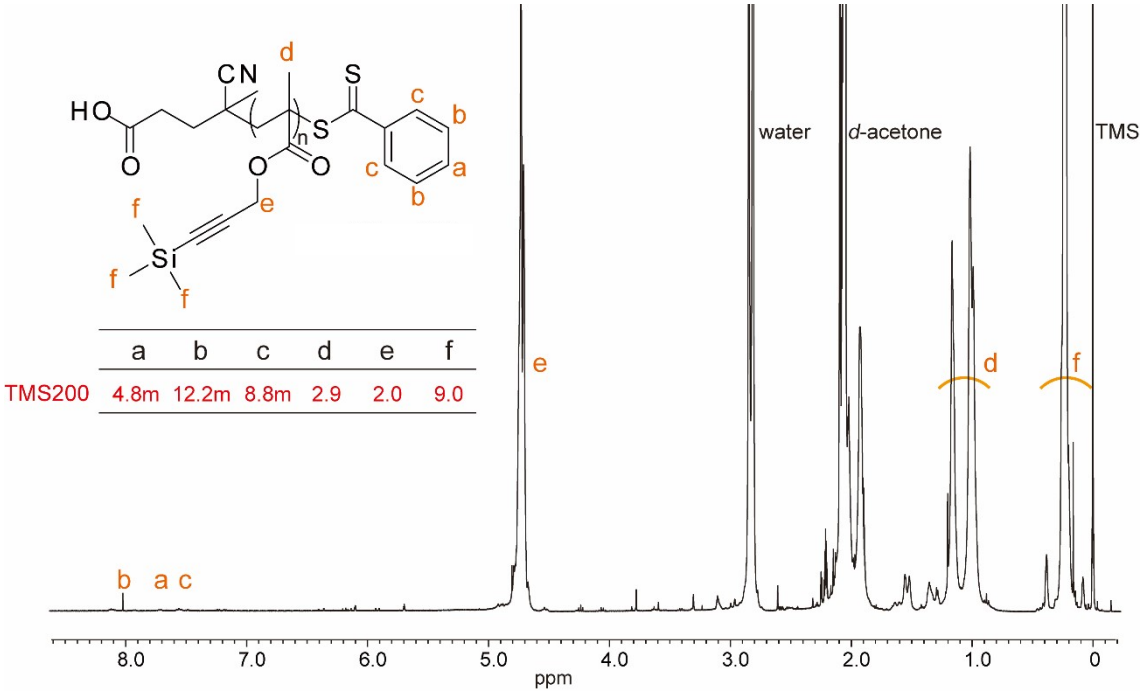
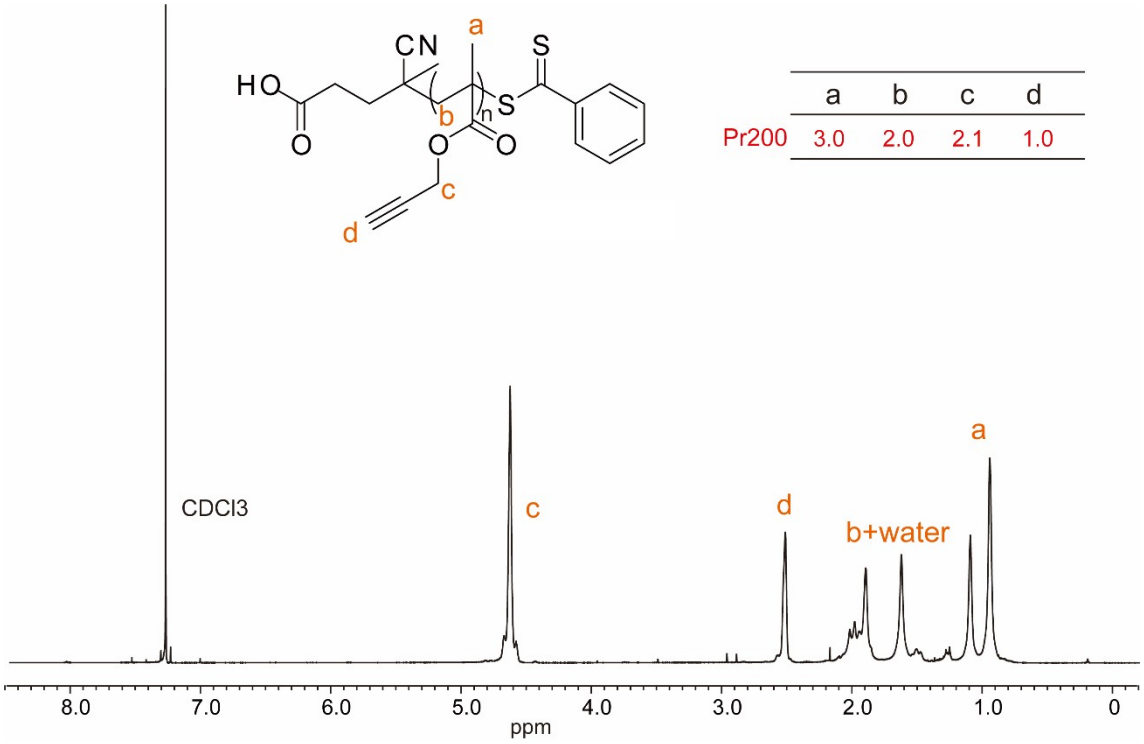
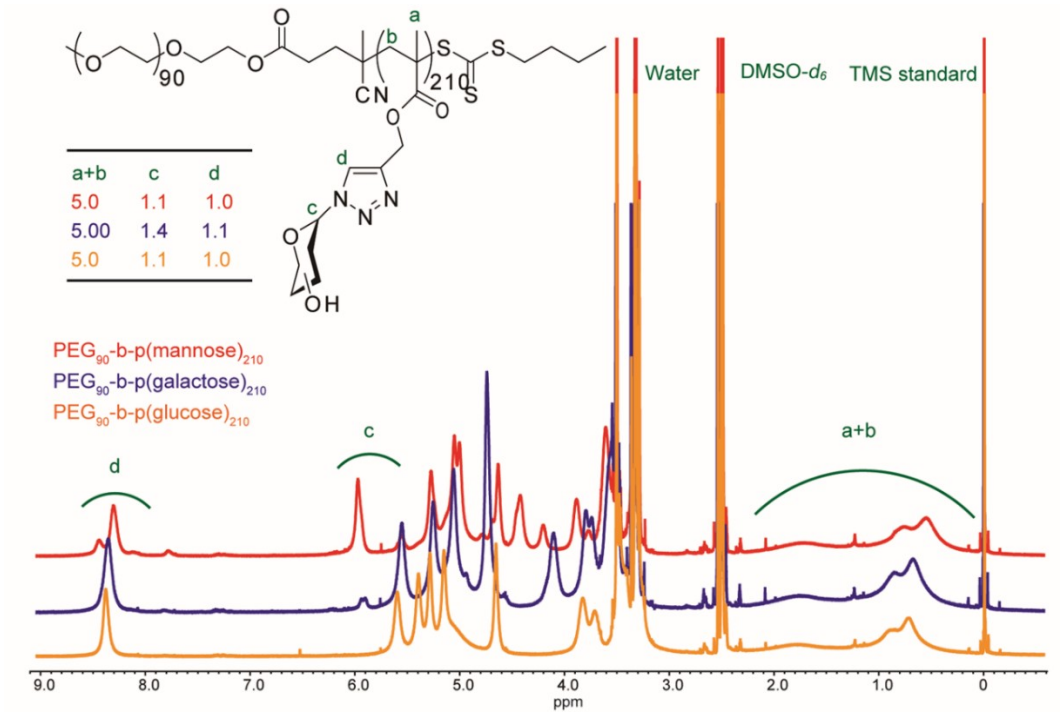



**Figure.S4- 6 $^{1}$H NMR of TMS200.**




| | a | b | c | d |
|---|---|---|---|---|
| Pr200 | 3.0 | 2.0 | 2.1 | 1.0 |

**Figure.S4- 7 $^{1}$H NMR of Pr200.**




| a+b | c | d |
|---|---|---|
| 5.0 | 1.1 | 1.0 |
| 5.00 | 1.4 | 1.1 |
| 5.0 | 1.1 | 1.0 |

**Figure.S4-8 $^{1}$H NMR after click reaction (red: $P_{90}Man_{200}$, blue: $P_{90}Gal_{200}$ and orange: $P_{90}Glc_{200}$).**

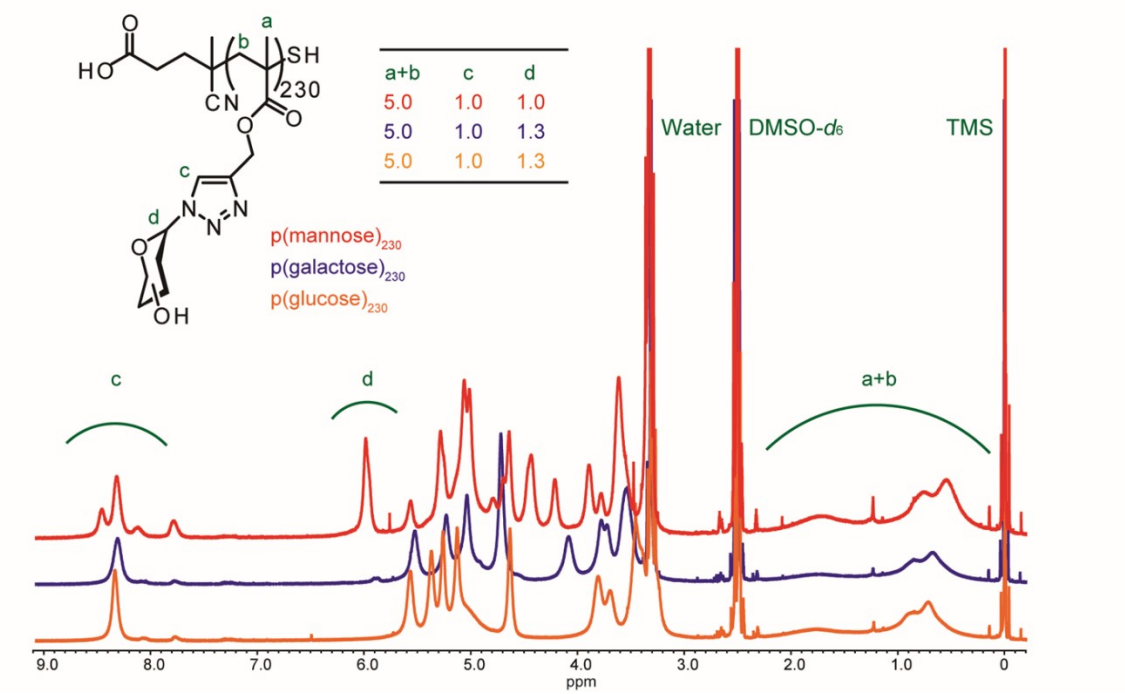



**Figure.S4- 9 $^{1}$H NMR after click reaction (red: $pMan_{200}$, blue: $pGal_{200}$ and orange: $pGlc_{200}$).**

## 5. GPC traces

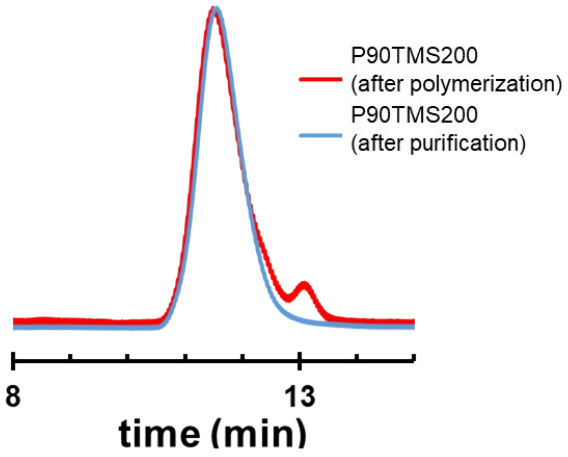



**Figure.S5- 1 GPC traces of P90TMS200 before and after purification.**

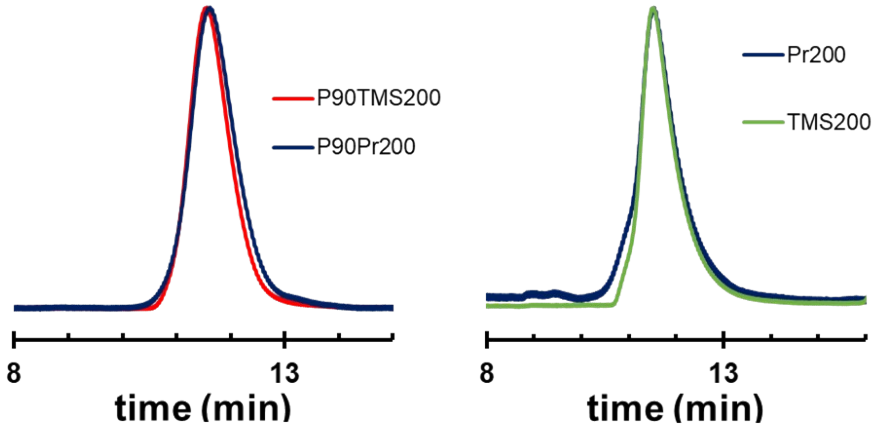



**Figure.S5- 2 GPC traces of P90TMS200, P90Pr200, TMS200 and Pr200.**

## 6. UV spectrum

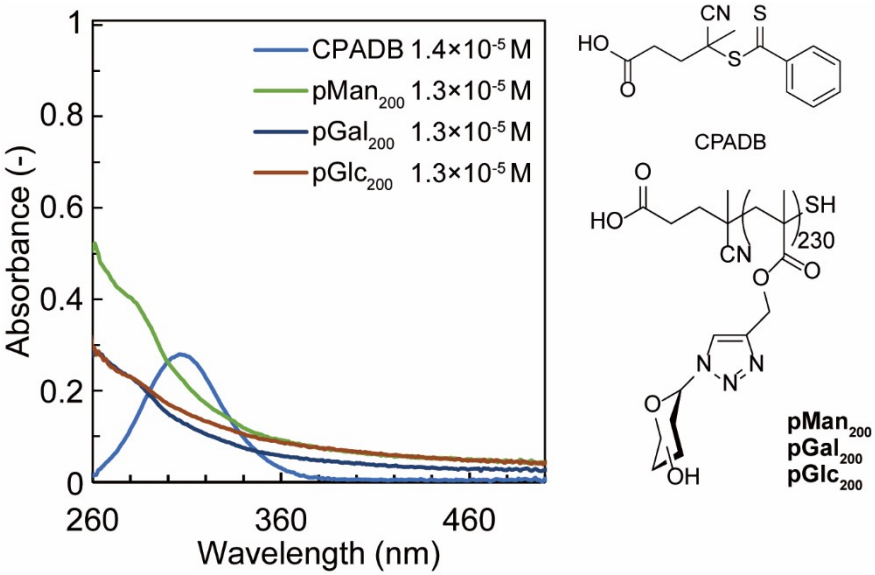
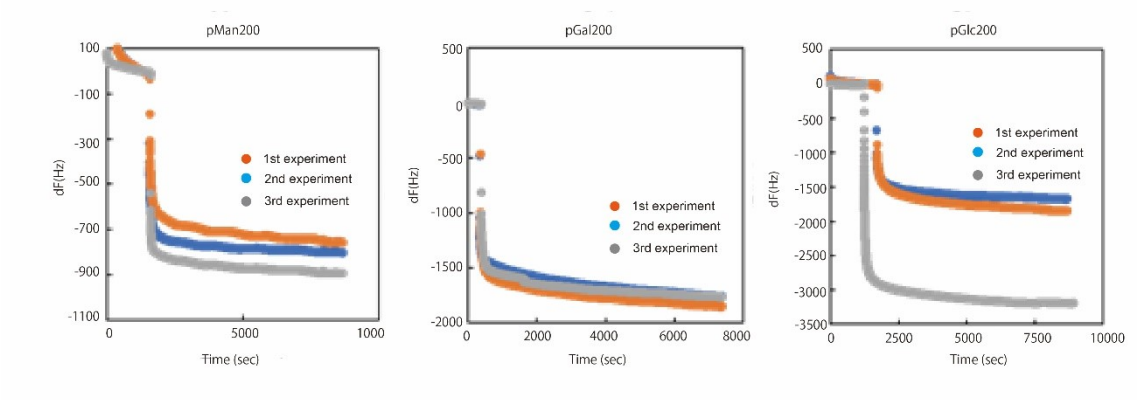
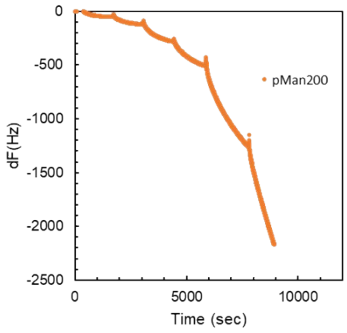



**Figure.S6- 1 UV spectrum of CPADB, $pMan_{200}$, $pGal_{200}$ and $pGlc_{200}$ in DMSO. The absorbance of 305 nm represents the dithio group. The absorbance of glycopolymers ($pMan_{200}$, $pGal_{200}$ and $pGlc_{200}$) was decreased, which indicated that the decomposed of dithio group of the glycopolymers.**

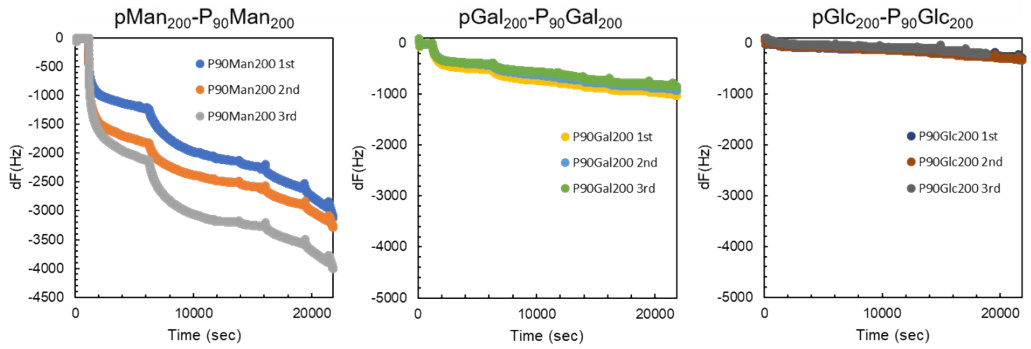
## 7. QCM measurement



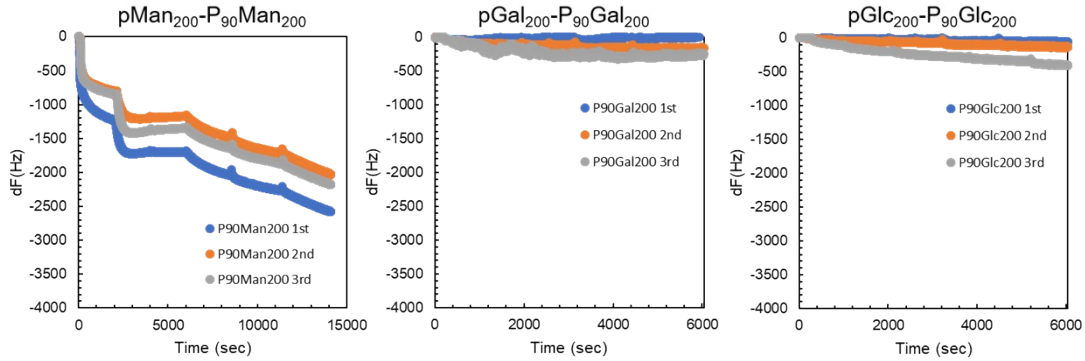

**FigureS7- 1 Immobilization glycopolymers ($pMan_{200}$, $pGal_{200}$ and $pGlc_{200}$) on the gold surface. Time course of frequency change QCM by adsorption of glycopolymers. (The QCM cell was placed in the QCM apparatus and monitored with 100 µL of Milli-Q until the frequency was constant. Once the frequency was constant, 100 µL of each glycopolymer ($pMan_{200}$, $pGal_{200}$ and $pGlc_{200}$) was added to bring the concentration in the cell to 10 g/L, and the cell was kept at 15ºC for 2 hours.)**



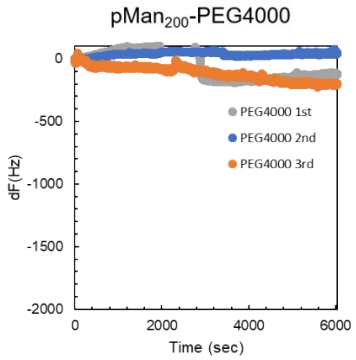

**FigureS7- 2 Frequency difference with injecting $pMan_{200}$ onto the $pMan_{200}$ immobilized gold surface. The adsorption at each concentration did not reach a steady state, due to the strong interaction of the mannose moiety, the polymer was stacked on the QCM substrate.**



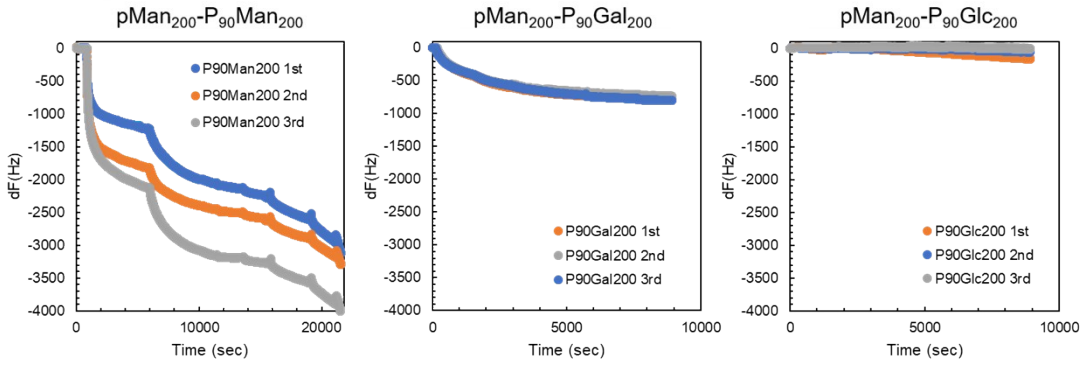

**FigureS7- 3 Frequency difference with injecting PEG-terminated glycopolymer ($P_{90}Man_{200}$, $P_{90}Gal_{200}$ and $P_{90}Glc_{200}$) onto the glycopolymer ($pMan_{200}$, $pGal_{200}$ and $pGlc_{200}$) immobilized gold surface.**



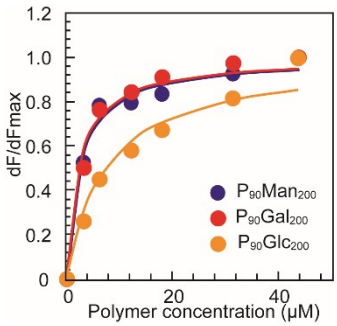

**FigureS7- 4 Frequency difference with injecting PEG-terminated glycopolymer ($P_{90}Man_{200}$, $P_{90}Gal_{200}$ and $P_{90}Glc_{200}$) onto the glycopolymer ($pMan_{200}$, $pGal_{200}$ and $pGlc_{200}$) immobilized gold surface without calcium ion.**



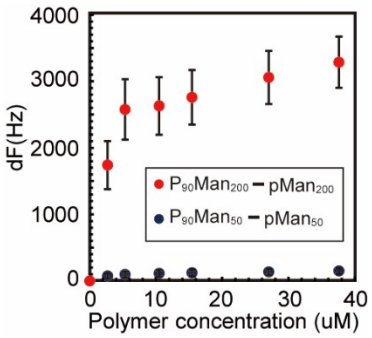

**FigureS7- 5 Frequency difference with injecting PEG onto the $pMan_{200}$ immobilized gold surface. There was no interaction between PEG and $pMan_{200}$.**




**FigureS7-6 Frequency difference with injecting PEG-terminated glycopolymer ($P_{90}Man_{200}$, $P_{90}Gal_{200}$ and $P_{90}Glc_{200}$) onto $pMan_{200}$ immobilized gold surface. The interaction between $pMan_{200}$ and $P_{90}Gal_{200}$ or $P_{90}Glc_{200}$ are much lower than that between $pMan_{200}$ and $P_{90}Man_{200}$.**




**FigureS7- 7 Langmuir fitting (right) by QCM measurement based on Fig.S7-3. Langmuir fitting was performed, with the assumption that the interaction between the glycopolymer moieties was a one-to-one binding.**




**FigureS7- 8 Frequency difference with injecting PEG-terminated glycopolymer ($P_{90}Man_{200}$ and $P_{90}Man_{50}$) onto $pMan_{200}$ or $pMan_{50}$ immobilized gold surface.**

## 8. XPS

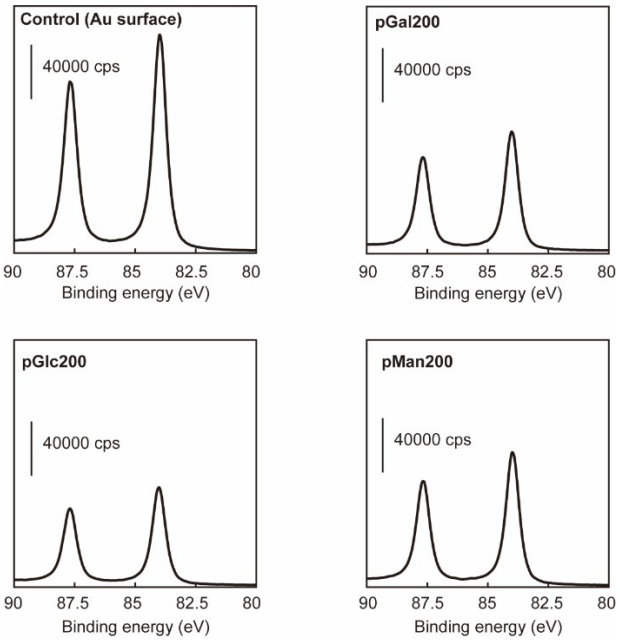



**Figure.S8- 1 XPS Au(4f) spectrum of A) bare, B) $pGal_{200}$ immobilized-, C) $pGlc_{200}$ immobilized-, and D) $pMan_{200}$ immobilized-gold surface. Au (4f) spectra of the unmodified gold surface was $1.6\times10^5$ (cps at 84.0 eV). On the other hand, Au (4f) spectra of each glycopolymer-immobilized gold surface were $9.8\times10^4$ (cps at 84.0 eV for $pMan_{200}$), $8.9\times10^4$ (cps at 84.0 eV for $pGal_{200}$) and $7.2\times10^4$ (cps at 84.0 eV for $pGlc_{200}$), respectively. In all cases, the Au peak decreased to the same extent.**

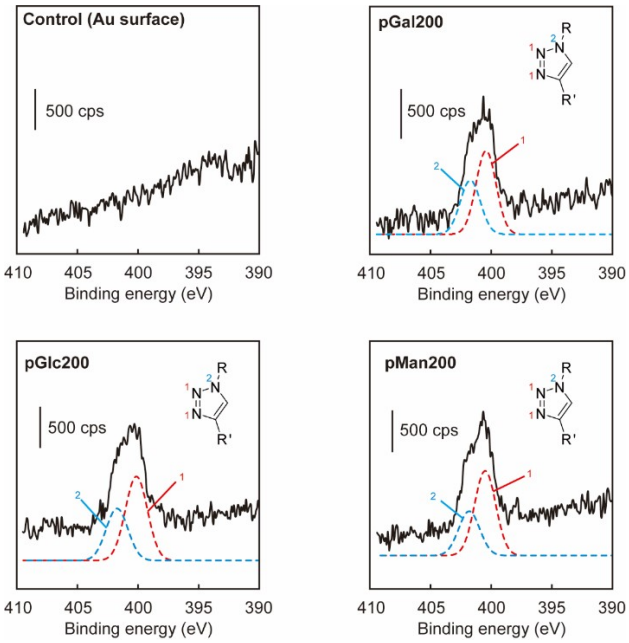



**Figure.S8- 2 XPS N(1s) spectrum of A) bare, B) $pGal_{200}$ immobilized-, C) $pGlc_{200}$ immobilized-, and D) $pMan_{200}$ immobilized-gold surface. In the N (1s) spectra of the unmodified gold substrate (AU surface), there are no peak corresponding to N=N (400.7 eV) and N-N (401.7 eV). In the N (1s) spectra of the $pMan_{200}$, $pGlc_{200}$ or $pGlc_{200}$-imobilized gold substrate, peaks corresponding to N=N and N-N were observed. These peak intensities of $pMan_{200}$-immobilized gold substrate are N=N ($10.2\times10^2$ cps) and N-N ($5.5\times10^2$ cps), respectively. In the case of $pGal_{200}$-immobilized gold substrate, these peak intensities are N=N ($8.1\times10^2$ cps) and N-N ($5.6\times10^2$ cps), respectively. In the case of $pGlc_{200}$-immobilized gold substrate, these peak intensities are N=N ($8.7\times10^2$ cps) and N-N ($6.6\times10^2$ cps), respectively.**

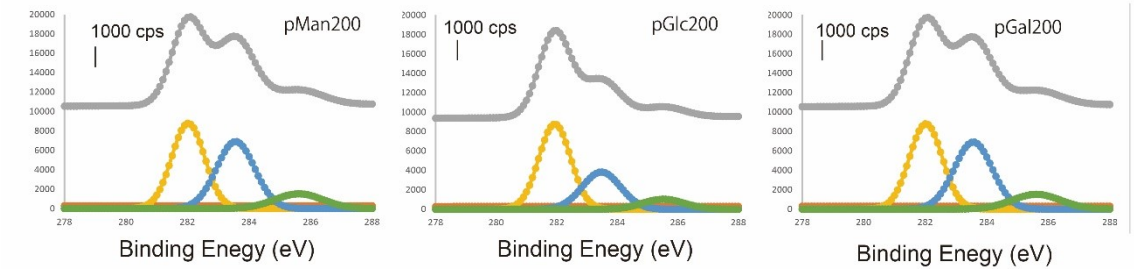



**Figure.S8- 3 XPS C(1s) spectrum of $pGal_{200}$ immobilized-, C) $pGlc_{200}$ immobilized-, and D) $pMan_{200}$ immobilized-gold surface. In the N (1s) spectra of the unmodified gold substrate (AU surface), there are no peak corresponding to N=N (400.7 eV) and N-N (401.7 eV). In the N (1s) spectra of the $pMan_{200}$, $pGlc_{200}$ or $pGlc_{200}$-imobilized gold substrate, peaks corresponding to C-C, C-H, C-O and C=O were observed.**

**9. Coordination bonding of mannose moieties**

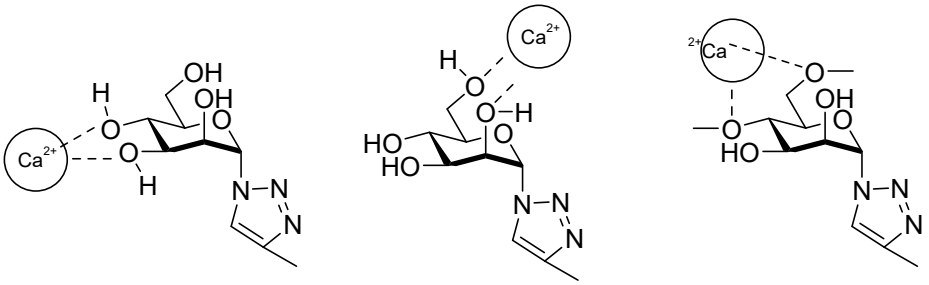



**Figure S11. The possible coordination bonding of mannose moieties based on a previous report. (J. Molecular Structure, 2001, 536, 227-234.)**