EFFECTIVE SYNTHESIS OF MAKING MANNOSE-BASED LINEAR AND TRULY
HYPERBRANCHED GLYCOPEOLYMER VIA REVERSE ATRP

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EFFECTIVE SYNTHESIS OF MAKING MANNOSE-BASED LINEAR AND TRULY HYPERBRANCHED GLYCOPOLYMER VIA REVERSE ATRP

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ii
ABSTRACT

Hyperbranched glycopolymers containing mannose units in the branch point were synthesized through the homopolymerization of a mannose-based inimer via atom transfer radical polymerization (ATRP). Incorporating a carbohydrate residue at the branch point may result in a closer analogue to natural branched polysaccharides. Characterization by gel permeation chromatography (GPC), both conventional GPC and light scattering GPC, can be used as an effective way to elucidate the characteristics of the hyperbranched polymer utilizing the mannose-based inimer as compared with the linear polymer. In my research work, I successfully synthesized linear glycopolymer and hyperbranched glycopolymer. Also, a reliable dn/dc value for this new type of glycopolymer was obtained. Another characterization method used was $^{1}$H NMR spectrometry.
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TABLE OF CONTENTS

LIST OF SCHEMES.............................................................................................................v
LIST OF FIGURES ........................................................................................................... vi
LIST OF TABLES ...............................................................................................................x

CHAPTER

I. INTRODUCTION ...............................................................................................................1

1.1 Oligo- and polysaccharides polymer system ...........................................................1

1.2 Synthetic route for Mannose-Based polymer and hyperbranched polymer...........3

II. LITERATURE REVIEW ................................................................................................4

2.1 Atom transfer radical polymerization (ATRP) .......................................................4

2.2 Variations of ATRP .................................................................................................5

III. EXPERIMENT SECTION .............................................................................................11

3.1 Materials ...............................................................................................................11

3.2 Techniques .............................................................................................................11

3.3 Synthetic procedures ............................................................................................12

3.3.1 Polymerization of (methyl acrylate) using normal ATRP ............................13

3.3.2 Polymerization of α, β 6-Acrylate-1, 2, 3, 4-tetraacetate mannopyranose via SARA ATRP .................................................................14

3.3.3 Polymerization of (2-Bromo-3-acryloyl-[α,β-6-O-1,2,3,4-tetraacetate mannopyranose] propionate) via SARA ATRP .................................................................15
3.3.4 Polymerization of α, β 6-Acrylate-1,2,3,4-tetraacetate mannopyranose via Reverse ATRP .......................................................... 16

3.3.5 Polymerization of ((2-Bromo-3-acryloyl-α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate) via Reverse ATRP .................................................. 17

IV. RESULT AND DISCUSSION ......................................................................................................................... 18

4.1 Synthesis of poly(methyl acrylate) .................................................................................................................. 18

4.2 Synthesis of poly(α,β-6-acrylate-1,2,3,4-tetraacetate mannopyranose) via SARA ATRP ................................................................. 20

4.3 Synthesis of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate) via SARA ATRP ................................................................. 21

4.4 Polymerization of α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose via Reverse ATRP ................................................................. 22

4.5 Polymerization of ((2-Bromo-3-acryloyl-[α,β-6-O-1,2,3,4-tetraacetate mannopyranose] propionate) via Reverse ATRP ................................................................. 25

V. CONCLUSION AND FUTURE WORK ......................................................................................................................... 31

REFERENCES .................................................................................................................................................. 33

APPENDIX ......................................................................................................................................................... 35
<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.1 Mechanism for traditional ATRP</td>
<td>5</td>
</tr>
<tr>
<td>2.2.1 Illustration of ARGET ATRP</td>
<td>6</td>
</tr>
<tr>
<td>2.3.1 The SARA ATRP Mechanism</td>
<td>8</td>
</tr>
<tr>
<td>2.4.1 The Reserve ATRP Mechanism</td>
<td>9</td>
</tr>
<tr>
<td>3.3.1 Synthetic route for poly (methyl acrylate)</td>
<td>13</td>
</tr>
<tr>
<td>3.3.2 Synthetic route for poly (α, β 6-Acrylate-1, 2, 3, 4-tetraacetate mannopyranose)</td>
<td>14</td>
</tr>
<tr>
<td>3.3.3 Synthetic route for poly (2-Bromo-3-acryloyl-[α, β -6O-1, 2, 3, 4-tetraacetate mannopyranose] propionate)</td>
<td>15</td>
</tr>
<tr>
<td>3.3.4 Synthetic route for poly (α, β 6-Acrylate-1, 2, 3, 4-tetraacetate mannopyranose)</td>
<td>16</td>
</tr>
<tr>
<td>3.3.5 Synthetic route for poly (2-Bromo-3-acryloyl-[α, β -6O-1, 2, 3, 4-tetraacetate mannopyranose] propionate)</td>
<td>17</td>
</tr>
<tr>
<td>4.1.1 Synthetic route for poly(methyl acrylate) ([M]/[CuBr]/[PMDETA]/[I] =100/1/1/1, 80°C,24h)</td>
<td>18</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure | Page
---|---
1.1.1 New class of linear and hyperbranched glycopolymer that has mannose incorporated as a pendant group | 2
4.1.1 300 MHz 1H NMR spectrum of poly(methyl acrylate) ([M]/[CuBr]/[PMDETA]/[I] =100/1/1/1, 80°C,24h) | 19
4.1.2 GPC trace of poly(methyl acrylate) produced by ATRP polymerization ([M]/[CuBr]/[PMDETA]/[I] =100/1/1/1, 80°C,24h) | 19
4.2.1 GPC trace of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) produced by SARA ATRP([M]/[I]/[Cu(0)]/[Me6TREN] =25/1/1/1, 25 oC,24 h) | 20
4.3.1 GPC trace of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate) produced by SARA ATRP([Inimer]/[Cu(0)]/[Me6TREN] =25/1/1/1, 25 oC,24 h) | 21
4.4.1 GPC of poly (α, β 6-Acrylate-1, 2, 3, 4-tetraacetate mannopyranose) after purification.([M]:[CuBr2]:[PMDETA]:[AIBN]=25:1:1:1, 110°C,72h) | 23
4.4.2 dn/dc value of poly( α , β -6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr2]:[PMDETA]:[AIBN]=25:1:1:1, 110°C,72h) | 23
4.4.3 light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr2]:[PMDETA]:[AIBN]=25:1:1:1, 110°C,72h) | 24
4.4.4 1H Spectrum of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr2]:[PMDETA]:[AIBN]=25:1:1:1, 110°C,72h) | 25
4.5.1 GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr2]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C,48h) | 26
4.5.2 dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr2]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C,48h) | 27
4.5.3 light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr2]:[PMDETA]:[AIBN]= 10:1:1:0.25, 110°C,48h) .................................................................................................................................28

4.5.4 ¹H Spectrum of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate) after purification. .........................................................................................................................29

4.6.1 Absolute molecular weight Vs Relative molecular weight for both linear and hyperbranched glycol-polymer ........................................................................................................................30
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.1 Polymerization of (α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) via Reverse ATRP</td>
<td>22</td>
</tr>
<tr>
<td>4.5.1 Polymerization of (2-Bromo-3-acryloyl-[α,β-6-O-1,2,3,4-tetraacetate mannopyranose] propionate) via Reverse ATRP</td>
<td>25</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

1.1 Oligo- and polysaccharides glycopolymer system

Oligo- and polysaccharides are well known as both energy sources and as structural materials. They can also play a significant role in biomedical processes such as viral entry,\(^1\) cell adhesion\(^2\) and pathogen recognition.\(^3\) However, so far, no effective synthetic route and characterization method have been demonstrated for well-defined oligo- and polysaccharides. Therefore the investigation of their roles in biology has been hindered. Generally, there are two approaches to synthesize glycol-polymers. First, a protection-deprotection sequence can be applied to synthesize oligo- and polysaccharides, but the yields are usually low. This is a good way to investigate the reactivity and binding affinity between glycopolymer and proteins, but definitely not a good way for producing a large quantity of biomaterials. The alternative way to make glycopolymers is to polymerize monomers containing a saccharide group. The advantage of this method is that it can produce high molecular weight polymer although it contains only one specific type of glycol- residue, and thus has limited specificity in biological interactions. Some
early research indicated that glycopolymer synthesis, polymeric sialoside, which was synthesized using post-polymerization modification of poly(4-nitrophenylacrylate)\(^4\) was able to hinder influenza virus attachment.\(^5\) After that, many synthetic methods for producing glycopolymers were developed.\(^6\)

In order to more fully capture natural polysaccharide structures, we synthesized a new class of linear and hyperbranched glycopolymers via atom transfer radical polymerization (ATRP) with glycomonomers and glycoinimers, in which the saccharide\(^7,8\) residues are incorporated as a pendant group (Figure 1.1). In this thesis, I will mainly describe the synthesis of a reactive monomer and an inimer that have mannose as a pendant group, and their polymerization via a different ATRP mechanism.\(^9\) Characterizations by HPLC and GPC can prove the formation of truly hyperbranched glycol-polymer structure.\(^10,11\)

![Figure 1.1](image)

Figure 1.1.1 New class of linear and hyperbranched glycopolymer that has mannose incorporated as a pendant group
1.2 Synthetic route for Mannose-Based polymer and hyperbranched polymer

Atom transfer radical polymerization (ATRP) has been widely used to polymerize a wide range of acrylic monomers to produce different well-defined polymers.\textsuperscript{12,13} Variations of ATRP have been investigated by researchers from many groups. ARGET ATRP differs from traditional ATRP, in that CuBr\textsubscript{2} is used as the catalyst in combination with a reducing agent such as ascorbic acid to generate CuBr. The use of an oxidatively stable catalyst precursor (CuBr\textsubscript{2}) makes the preparation, shipment and storage of ATRP catalyst systems much easier. The hyperbranched architecture and the connectivity of a saccharide into a glycopolymer can significantly affect the properties of the glycopolymer with respect to its linear analogs. While ARGET ATRP has been used by my groupmate, it always results in very low conversion and very low yield. Therefore, I chose reverse ATRP to improve the conversion and yield of this reaction.
2.1 Atom transfer radical polymerization (ATRP)

ATRP is a controlled radical polymerization that is controlled by a dynamic equilibrium between propagating radicals and dormant species. The reaction begins with activation of an alkyl halide dormant species (PnX) by reacting with a transition metal complex in its lower oxidation state (Mt\textsuperscript{m}/L, where Mt\textsuperscript{m} represents the transition metal species, usually copper can be used, m represents oxidation state and L represents the ligand being used). The redox reaction between PnX and Mt\textsuperscript{m} generates a radical species (Pn\textsuperscript{+}) with a rate constant of activation, \(k_{\text{act}}\). This reaction is in equilibrium with reformation of the dormant species from the higher oxidation state transition metal complex (X-Mt\textsuperscript{m+1}/L) containing the coordinated halide; this reverse reaction occurs with a rate constant of deactivation, \(k_{\text{deact}}\) (Scheme 2.1). The living radicals, Pn\textsuperscript{+}, add vinyl monomer with a rate constant of propagation (\(k_p\)) until they irreversibly terminate by unavoidable radical-radical coupling with rate constant of termination (\(k_t\)).
As shown in eq 1, the reaction rate of an ATRP ($R_p$) depends on the rate constant of propagation reaction ($k_p$) and the concentration of monomers $[M]$ and propagating species $[Pn']$.

$$R_p = k_p[M][Pn'] \quad (eq \ 1)$$

The concentration of radicals depends on the ATRP equilibrium constant and the concentration of dormant species $[PnX]$, activators $[Mt^m/L]$, and deactivators $[Mt^{m+1}/L]$. (Eq. 2 ignores chain transfer and termination.)

$$[Pn'] = \frac{k_{act}[PnX][Mt^m/L]}{k_{deact}[Mt^{m+1}/L]} \quad (eq \ 2)$$

As shown in eq 3, from combination of eq 1 and eq 2, the reaction rate of ATRP depends on the overall equilibrium constant ($K_{ATRP}$).

$$R_p = k_p K_{ATRP} \frac{[PnX][Mt^m/L][M]}{[Mt^{m+1}/L]} \quad (eq \ 3)$$

2.2 Variations of ATRP

ATRP has some limitations. Since ATRP is initiated by a redox reaction between an R-X initiator and a catalyst complex in a lower oxidation state, the transition metal
complexes may be easily oxidized to a higher oxidation state. Therefore, the preformed catalysts must be stored under an inert atmosphere. Oxygen and other oxidants must be removed from the system prior to the addition of the catalyst in the lower oxidation state.\textsuperscript{16}

With the development of ATRP, starting with roughly equivalent concentrations of R–X and the lower oxidation state catalyst (\(M_t^n/L\)), a “reverse” ATRP mechanism was proposed that begins by addition of the higher oxidation state transition metal complex (X–\(M_t^{n+1}/L\)), which is then converted to the activator (\(M_t^n\)) by reaction with a standard free radical initiator, using various reducing agents including \(M_t^0\) species. This was first proposed by Matyjaszewski et al. and named activators generated by electron transfer (AGET),\textsuperscript{17} and various reducing agents. This was followed by the approach of continuously regenerating a small amount of catalyst as in AGET, and was named activator regenerated by electron transfer (ARGET) (Scheme 2).\textsuperscript{18}

\[
\begin{align*}
R-X + Mt^n/L & \xrightarrow{k_{act}} Mt^{n+1}X/L + R- \\
& \xrightarrow{k_{deact}} Mt^n/L + R-X \xrightarrow{k_t} M + R-R
\end{align*}
\]

\text{ARGET} \quad \text{Oxidized Agent} + \text{HX} \quad \text{Excess Reducing Agent}

Scheme 2.2.1 illustration of ARGET

These techniques have all of the advantages of a normal ATRP reaction. The use of an oxidatively stable catalyst system makes the preparation, storage, and transportation of
ATRP catalyst systems much easier.\textsuperscript{19} Furthermore, Cu(II) is much less expensive than Cu(I), which makes this reaction more economically favorable.

However, Cu(II) catalyst complexes are generally less soluble than Cu(I) catalyst complexes in organic media, which often results in heterogeneous polymerizations. For conventional ATRP, highly active catalysts system at concentrations $[\text{Cu (I)}]/[\text{RX}] \leq 0.1$, and lower reaction temperature are required to observe a “living” behavior. For AGET or ARGET ATRP, the higher oxidation state Cu(II) will be reduced to lower oxidation state Cu(I) in the presence of the appropriate reducing agents, such as FDA-approved tin(II) 2-ethylhexanoate (Sn(EH)\textsubscript{2}), L-ascorbic acid, phenol, hydrazine, with excess inexpensive ligands, like $N,N',N'',N'''$-pentamethyldiethylenetriamine (PMDETA) and Tris[2-(dimethylamino)ethyl]amine (Me\textsubscript{6}TREN), nitrogen-containing monomers, or Cu(0). With the use of reducing agents, the oxidatively stable Cu(II) species can be used in the reaction. The reducing/reactivating cycle can also be applied to eliminate air, or other radical traps in the system.

Recently, supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP)\textsuperscript{19} was introduced by Dr. Krzysztof Matyjaszewski to explain the fast polymerization of acrylic monomer with Cu(0) as catalyst and in the presence of DMSO. The proposed mechanism for SARA ATRP is shown in Scheme 2.3.
Scheme 2.3.1 The SARA ATRP Mechanism

In this case, the author demonstrated that the Cu(0) act as the supplemental activator for alkyl halide in the presence of polar solvent, as long as the Cu(I) is consumed.

SARA ATRP was proposed to explain the fast polymerization of acrylic monomers such as methyl methacrylate in polar solvents such as DMSO or water with the presence of Cu(0) and ligands that generate active Cu catalyst complexes. Scheme 2.3 shows the possible reaction scheme between the metallic species, various oxidation states of copper, and alkyl halides, as well as the propagating species and metallic species. The comproportionation of Cu(0) and Cu(II) species with reaction rate coefficient $k_{comp}$ can generate two Cu(I) species, and the disproportionation of Cu(0) and Cu(II) is also possible with rate coefficient $k_{disp}$. The lower oxidation state copper complex (Cu(0) and Cu(I)) can activate alkyl halides to give the copper higher oxidation state and generate propagating species with rate coefficients $k_{a0}$ and $k_{a1}$. The higher oxidation state copper complex (Cu(II)), can deactivate radicals to give the copper lower oxidation state and regenerate the alkyl halide with rate coefficient $k_{d0}$ and $k_{d1}$. The structure of the reagents
such as initiators, ligands, monomers may also influence the SARA ATRP reaction. And also, the temperature, polarity and pressure will influence the whole equilibrium.

In a "reverse" ATRP the components that are added to the reaction system are less sensitive to air; therefore the catalyst complex is easier to prepare during the addition of reactants, and the procedure was thought to be more compatible with industrial scale processes since standard free radical initiators are employed. It means that the initiation process does not proceed by the activation of an alkyl halide with a $M_t^{n}/L$ catalyst. Instead, it proceeds by the thermal decomposition of a conventional free radical initiator such as AIBN. Once free radicals are generated, they either react with the higher oxidation state copper complex to generate the lower oxidation state copper complex and a dormant species, $I \cdot + X-M_t^{n+1}/L$ forming $I-X + M_t^{n}/L$, or they react with monomer to generate a propagating species, $I-P_1\cdot$, which will be quickly deactivated by reaction with the added $X-M_t^{n+1}/L$ to form $M_t^{n}/L$ and a dormant species, $I-P_1-X$.

**Scheme 2.4.1 The Reserve ATRP Mechanism**
In this case, reserve ATRP can significantly improve the conversion and yield for this polymerization. I can significantly improve the initiation efficiency of this reaction since a normal free radical initiator is much more reactive and easily decomposed, which will ensure the formation of ATRP initiator. The propagation procedure is the same as normal ATRP.
CHAPTER III

EXPERIMENT SECTION

3.1 Materials

Azobisisobutyronitrile (AIBN) (Aldrich, purity 99%), Cu(0) (Aldrich, purity 99%), CuBr (Aldrich, purity 99%), Dimethyl sulfoxide (DMSO) (Aldrich, purity 99%), L-Ascorbic Acid (fisher scientific, purity 99%), methyl acrylate (Aldrich, purity 99%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (Aldrich, purity 99%), water (distilled), were used as received. Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was synthesized by Xiang Yan (book II 32(b) 2-25-14).

Purification: CuBr was purified by stirring it in glacial acetic acid overnight, washing it several times with methanol, and then drying.²¹

3.2 Techniques

Schlenk line: All reactions were performed under a N₂ atmosphere using a Schlenk line unless noted otherwise.
Freeze-pump-thaw cycles: Freeze the Schlenk tube in liquid nitrogen for 5 mins then put it under vacuum for 15 or 30 min. Closing the Schlenk tube and let is thaw to room temperature in methanol and then towel-dry the Schlenk tube. Cycle the process until there are no decavitation bubbles formed when thawing the Schlenk tube to room temperature.

NMR Spectroscopy: $^1$H (δ, ppm) NMR spectroscopy was recorded on a Varian Mercury 300 (300 MHz) instrument. Unless noted otherwise, all spectra were recorded in CDCl$_3$, and the resonances were measured relative to residual solvent resonances and referenced to tetramethylsilane (0.00 ppm).

GPC: Number-average ($M_n$) and weight-average ($M_w$) molecular weights relative to linear polystyrene (GPC$_{PS}$) and polydispersities (PDI=$M_w/M_n$) were determined by gel permeation chromatography (GPC) from calibration curves of $\log M_n$ vs elution volume at 35 °C using THF (unless noted otherwise) as solvent (1.0 mL/min), a guard column and set of 50 Å, 100 Å, $10^4$ Å, and linear (50-10$^4$ Å) Styragel 5 μm columns, a Waters 486 tunable UV/vis detector set at 254 nm, a Waters 410 differential refractometer, and Millenium Empower 2 software. The samples (∼0.1 g/L) were dissolved overnight and filtered through a 0.45 μm PTFE filter.

3.3 Synthetic procedures

Different synthetic procedures have been figured out to make both linear and hyperbranched glycopolymer via the following synthetic methods.
3.3.1 Polymerization of (methyl acrylate) using normal ATRP (Scheme 3.3.1)

Scheme 3.3.1 Synthetic route for poly(methyl acrylate)

In a typical procedure, CuBr was added under a stream of nitrogen to the Schlenk tube and the Schlenk tube was set under vacuum for 30 minute, then PMDETA (21.6 mg, 12.4 mmol) in acetonitrile (0.5 mL) was added into the Schlenk tube. The system was degased by freeze (5 min)-pump (20 min)-thaw (5 min) twice. Then Schlenk tube was set under flowing N₂, and methyl acrylate (1.06 g, 11.5 mmol) was added into the Schlenk tube. The system was degased by freeze (5 min)-pump (20 min)-thaw (5 min) twice again. 0.0219 g 2-((2-bromo-2-methylpropanoyl)oxy)ethan-1-ylidene was added into another small vial, then degased by freeze(5min)–pump(20min)–thaw(5min) three times. The Schlenk tube was set in oil bath, the polymerization mixture was stirred at 80 ℃ for 72 hours. The system became very viscous and the stir bar was unable to stir anymore. Then the Schlenk tube was set into a dewar flask that contained liquid N₂ to quench the polymerization and opened the glass stopper at the same time, the contents of the polymerization tube were thawed, exposed to the atmosphere. Then THF was used to solvate the system and passing through basic alumina to remove copper complex and precipitated from methanol(60 mL) twice to yield 425 mg (40.1%) poly(methyl acrylate) as a slightly yellow viscous liquid: $M_n=7.56\times10^3$ g/mol, $pdi=1.13$
3.3.2 Polymerization of α, β 6-Acrylate-1, 2, 3, 4-tetraacetate mannopyranose via SARA ATRP (Scheme 3.3.2)

In a typical procedure, Cu (6.4 mg, 0.1 mmol) was added into the Schlenk tube, then the Schlenk tube was set under vaccum. Me₆TREN/DMSO (0.18 mL, 0.1086 mol/L) was added and degased by freeze(5 min)-pump(20 min)-thaw(5 min) twice, monomer(0.2 g, 0.5 mmol) and initiator/DMSO(0.334 mL, 0.0596 mol/L) were added into the Schlenk tube and degased by freeze(5 min)-pump(20 min)-thaw(5 min) three times. The Schlenk tube was set in oil bath (25°C). 2 hours later, the polymerization was quenched by setting the Schlen tube in liquid N₂, then the system was solvated with CH₂Cl₂ and passed through basic alumina to remove copper complex twice. The system was redissolved in 0.8 mL CH₂Cl₂ and precipitated from methanol(8 mL) twice to yield 24.2 mg (12.1%) poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) as a white powder : Mₙ= 5.64×10³ g/mol, pdi=1.31

Scheme 3.3.2 Synthetic route for poly ( α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose)
3.3.3 Polymerization of ((2-Bromo-3-acryloyl-[^α,β-6-O-1,2,3,4-tetraacetate mannopyranose] propionate) via SARA ATRP (Scheme 3.3.3)

In a typical procedure, Cu (5.72 mg, 0.8 μmol) and Me₆TREN/DMSO stock solution (0.0434 mol/L, 0.5 mL) were added into a 25mL Schlenk tube and degased by freeze (5 min)-pump (20 min)-thaw (5 min) twice to the Schlenk tube. Inimer(in 0.2 mL DMSO)(0.363 mmol) was added into the Schlenk tube and degased by freeze(5 min)-pump(20 min)- thaw(5 min) three times. The Schlenk tube was set in oil bath (25°C). 2 hours later, the polymerization was quenched by setting the Schlenk tube in liquid N₂. 5 mL CH₂Cl₂ was used to solvate the system and passed through basic alumina to remove copper complex twice. The system was redissolved in 0.8 mL CH₂Cl₂ and precipitated from methanol(8 mL) twice to yield 24.2 mg (12.1%) poly (2-Bromo-3-acryloyl-[^α, β-6O-1,2,3,4-tetraacetate mannopyranose] propionate) as a white powder : Mₙ= 5.79×10³ g/mol, pdi=1.24

![Scheme 3.3.3 synthetic route for poly(2-Bromo-3-acryloyl-[α,β-6-O-1,2,3,4-tetraacetate mannopyranose] propionate)](image-url)
3.3.4 Polymerization of α, β 6-Acrylate-1,2,3,4-tetraacetate mannopyranose via Reverse ATRP (Scheme 3.3.4)

In a typical procedure, CuBr₂/PMDETA/acetonitrile (0.035 mL, 0.0906 mol/L) was added into the Schlenk tube, the Schlenk tube was set under vaccum, mannose-based monomer (0.94 mmol, dissolved in 0.3 mL anisole) was added into the Schlenk tube, and degased by freeze(5 min)-pump(10 min)-thaw(5 min) three times. AIBN (9.4 μ mol, added as solid) was added into the Schlenk tube, and degased by freeze(5 min)-pump(10 min)-thaw(5 min) five times to the Schlenk tube. 72 hours later, the polymerization was quenched by setting the Schlenk tube in liquid N₂, then use THF to dissolve it and passed through basic alumina to remove copper complex twice. The system was redissoved in 0.8 mL THF and precipitated from methanol(8 mL) twice to yield 201 mg (66.8%) poly(α,β 6-Acrylate-1,2,3,4-tetraacetate mannopyranose) as white powder: Mₙ= 4.5×10³ g/mol, pdi=1.28.

![Scheme 3.3.4 Synthetic route for poly (α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose)](image)

Scheme 3.3.4 Synthetic route for poly (α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose)
3.3.5 Polymerization of (2-Bromo-3-acryloyl-\([\alpha,\beta-6\text{-O-1,2,3,4-tetraacetate }\text{mannopyranose}]\) propionate) via Reverse ATRP (Scheme 3.3.5)

In a typical procedure, CuBr$_2$/PMDETA/acetonitrile (0.15 mL, 0.0469 g/mL) was added into the schlenk tube, the Schlenk tube was set under vaccum, mannose-based bromo-inimer (0.4 mmol, dissolved in 0.3 mL anisole) was added into the Schlenk tube. The system was degased by freeze(5 min)-pump(10 min)-thaw(5 min) three times. AIBN (9.4 $\mu$ mol, added as solid) was added into the Schlenk tube, and the contents were degased by freeze(5 min)-pump(10 min)-thaw(5 min) five times. After 2 days, the polymerization was quenched by setting the Schlenk tube in liquid N$_2$, then THF was used to dissolve the system and passed through basic alumina to remove copper complex twice. The system was redissolved in 0.8mL THF and precipitated from methanol(8 mL) twice to yield 124 mg (56.8%) poly(2-Bromo-3-acryloyl-\([\alpha,\beta-6\text{-O-1,2,3,4-tetraacetate }\text{mannopyranose}]\) propionate) as white powder: $M_n= 6.02 \times 10^3$ g/mol, $pdi=1.52$.

Scheme 3.3.5 Synthetic route for poly(2-Bromo-3-acryloyl-\([\alpha,\beta-6\text{-O-1,2,3,4-tetraacetate }\text{mannopyranose}]\) propionate)
4.1 Synthesis of poly(methyl acrylate)

As outlined in Scheme 4.1, the poly(methyl acrylate) was synthesized by following traditional ATRP method. I did this experiment to practice how to do ATRP reaction. I acquired techniques of doing ATRP through this reaction. This reaction was successful.

Scheme 4.1.1 Synthetic route for poly(methyl acrylate) ([M]/[CuBr]/[PMDETA]/[I] =100/1/1/1, 80°C, 24h)

Methyl acrylate was polymerized by traditional ATRP using [M]/[CuBr]/[PMDETA]/[I] =100/1/1/1 in acetonitrile at 80°C as conditions according to Scheme 4.1. Figure 4.1.1 presents the $^1$H NMR spectrum of this polymer. The vinyl resonances at 5.5-6.8 ppm have completely disappeared, which indicates that the purification was successfully and unreacted monomer can be removed. The broad
resonances also confirm that a polymer was generated. Figure 4.1.2 presents the corresponding GPC trace of this polymer. According to this GPC trace, $M_n=7.56\times10^3$ and PDI=1.13. The theoretical molecular weight should be $M_n=8.6\times10^3$, and the practical molecular weight is pretty close to this number but not exactly the same. This could be due to the unreacted monomer, which indicates that the conversion was not 100%.

![Figure 4.1.1 300 MHz $^1$H NMR spectrum of poly(methyl acrylate) ([M]/[CuBr]/[PMDETA]/[I] =100/1/1/1, 80°C, 24h)](image)

Figure 4.1.1 300 MHz $^1$H NMR spectrum of poly(methyl acrylate) ([M]/[CuBr]/[PMDETA]/[I] =100/1/1/1, 80°C, 24h)
Figure 4.1.2 GPC trace of poly(methyl acrylate) produced by ATRP polymerization ([M]/[CuBr]/[PMDETA]/[I] =100/1/1/1, 80 °C, 24h)

4.2 Synthesis of poly(α,β-6-acrylate-1,2,3,4-tetraacetate mannopyranose) via SARA ATRP

α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose was polymerized by SARA ATRP using [M]/[I]/[Cu(0)]/[Me₆TREN] =25/1/1/1 in DMSO at 25 °C for 24 hours. Figure 4.3 shows that the $M_n = 5.64 \times 10^3$ g/mol, pdi=1.32. The theoretical molecular weight should be around $1 \times 10^4$, but the practical molecular weight was almost half of it, which indicates that the conversion of monomer was so low, only half of the monomer was reacted. Perhaps longer reaction time will significantly improve the conversion. This reaction gave me very low yield after precipitation so that I could not take the $^1$H NMR for the refined product.
Figure 4.2.1 GPC trace of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) produced by SARA ATRP ([M]/[I]/[Cu(0)]/[Me₆TREN] = 25/1/1/1, 25 °C, 24 h)

4.3 Synthesis of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate) via SARA ATRP

2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate was polymerized by SARA ATRP using [Inimer]/[Cu]/[Me₆TREN] = 25/1/1 in DMSO at 25°. Figure 4.3 shows that the $M_n = 5.79 \times 10^3$ g/mol, pdi=1.23. I did not expect a specific number for number average molecular weight because in theory every inimer was an initiator and was able to initiate polymerization, but the practical molecular weight was too low, which indicates that the conversion of inimer was so low, and maybe the product was not hyperbranched polymer. The region between 45mins and 54mins indicates some oligomers with low molecular weight. This reaction gave me very low yield after precipitation so that I could not take the $^1$H NMR for the refined product.
Figure 4.3.1 GPC trace of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate) produced by SARA ATRP([Inimer]/[Cu(0)]/[Me$_6$TREN] =25/1/1/1, 25 °C ,24 h)

4.4 Polymerization of α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose via Reverse ATRP

Table 4.4 summarizes conversion, yield, relative molecular weight, absolute molecular weight and dn/dc value for linear polymer with different molecular weight. In order to control the molecular weight, different molar ratio between each reactant were applied.

Table 4.4.1 Polymerization of α(β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) via Reverse ATRP

<table>
<thead>
<tr>
<th>[M]:[CuBr$_2$]:[PMDETA]:[AIBN]</th>
<th>yield %</th>
<th>Mn(kDa)/GPC PDI/GPC</th>
<th>Mn(kDa)/LS PDI/LS</th>
<th>dn/dc</th>
</tr>
</thead>
<tbody>
<tr>
<td>25:1:1:1</td>
<td>70</td>
<td>4.5 1.28</td>
<td>9.8 1.21</td>
<td>0.061±(4.38%)</td>
</tr>
<tr>
<td>40:1:1:1</td>
<td>50</td>
<td>8 1.57</td>
<td>21.5 1.31</td>
<td>0.059±(2.02%)</td>
</tr>
<tr>
<td>50:1:1:1</td>
<td>57</td>
<td>10.1 1.48</td>
<td>27.5 1.25</td>
<td>0.068±(3.28%)</td>
</tr>
<tr>
<td>100:1:1:1</td>
<td>52</td>
<td>20.8 2.03</td>
<td>52.1 1.55</td>
<td>0.060±(1.12%)</td>
</tr>
</tbody>
</table>

Figure 4.4.1 shows the GPC data of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 25:1:1:1. The theoretical molecular weight for this polymer should be around 4.6×10$^3$, and the practical molecular weight was pretty close to that. It means that the conversion was very high and the initiation efficiency was pretty good.
Figure 4.1 GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=25:1:1:1, 110°C, 72h)

Figure 4.2 shows the dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 25:1:1:1. The result looks perfect with very low error(±4.38%). Since I created a new type of glycopolymer, I measured the dn/dc value for all the other samples and they look pretty good also. Those figures can be found in the appendix.
Figure 4.4.2 dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=25:1:1:1, 110°C, 72h)

Figure 4.4.3 shows the light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 25:1:1:1. Based on the dn/dc value, the absolute molecular weight is $9.8 \times 10^3$ with pdi=1.21. Other results for reactions with different mole ratio can be found in the appendix.

Figure 4.4.3 light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=25:1:1:1, 110°C, 72h)

Figure 4.4.4 shows the $^1$H NMR spectrum of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. The spectrum looks very good except for the peak from methanol. I should have put the sample in vaccum oven for longer time in order to remove methanol completely.
Figure 4.4.4 $^1$H Spectrum of poly($\alpha,\beta$-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=25:1:1:1, 110°C, 72h)

4.5 Polymerization of (2-Bromo-3-acryloyl-$\alpha,\beta$-6-O-1,2,3,4-tetraacetate mannopyranose] propionate) via Reverse ATRP (Scheme 3.3.5)

The following figure (table 4.5) summarizes conversion, yield, relative molecular weight, absolute molecular weight and dn/dc value for hyperbranched polymer with different molecular weight. In order to control the molecular weight, different reaction time were applied.

Table 4.5.1 Polymerization of 2-Bromo-3-acryloyl-$\alpha,\beta$-6-O-1,2,3,4-tetraacetate mannopyranose] propionate) via Reverse ATRP

<table>
<thead>
<tr>
<th>[M]:[CuBr$_2$]:[PMDETA]:[AIBN] yield %</th>
<th>Mn(kDa)/GPC</th>
<th>PDI/GPC</th>
<th>Mn(kDa)/LS</th>
<th>PDI/LS</th>
<th>dn/dc</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:1:1:0.25 48 hours</td>
<td>51</td>
<td>6.02</td>
<td>1.52</td>
<td>47.07</td>
<td>1.23</td>
</tr>
<tr>
<td>60 hours</td>
<td>60</td>
<td>8.08</td>
<td>1.6</td>
<td>57.08</td>
<td>1.37</td>
</tr>
<tr>
<td>72 hours</td>
<td>66</td>
<td>12.71</td>
<td>2.08</td>
<td>113.3</td>
<td>1.43</td>
</tr>
<tr>
<td>84 hours</td>
<td>73</td>
<td>14.64</td>
<td>2.22</td>
<td>130.1</td>
<td>1.29</td>
</tr>
<tr>
<td>96 hours</td>
<td>77</td>
<td>18.12</td>
<td>2.1</td>
<td>182.3</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Figure 4.5.1 shows the GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-
tetraacetate mannopyranose)) after purification. The reaction time was 48 hours and I
expected the polymer to have low molecular weight. The results turned out to be good.
Other results for reactions with different reaction time can be found in appendix.

Figure 4.5.1 GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr₂]:[PMDETA]:[AIBN]=10:1:1:0.25,
110°C,48h)

Figure 4.5.2 shows the dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-
tetraacetate mannopyranose)) after purification. The result looks perfect with very low
error(±3.92%). Since I created a new type of glycopolymer, I measured dn/dc value for
all the other samples and they look pretty good also. Those figures can be found in the
appendix.
Figure 4.5.2 dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 48h)

Figure 4.5.3 shows the light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. Based on the dn/dc value, the absolute molecular weight is 4.7x10$^4$ with pdi=1.23. Because of the hyperbranched property, the absolute molecular weight was way higher than the relative molecular weight for hyperbranched polymer. Other results for reaction with different reaction time can be found in the appendix.
Figure 4.5.3 light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr_2]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 48h)

Figure 4.5.4 shows the ^1H NMR spectrum of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose) propionate) after purification. Region(4.5ppm-4.2ppm) indicates that the polymer has not been eliminated by the ligand, which indicates the procedure in preparing the reaction system was correct and has no risk in causing β-hydrogen elimination. Region(6.0ppm) indicates that there are some unreacted vinyl groups in the hyperbrached polymer.
Table 4.4 and 4.5 summarize the characterization data for both the linear and hyperbranched polymers. Based on the data from table 4.4 and 4.5, a plot of the absolute molecular weight vs. the relative molecular weight can be made. As shown in Figure 4.6, the hyperbranched glycopolymer has much higher absolute molecular weight than its relative molecular weight (relative to polystyrene standard). The possible explanation is that conventional GPC calculates the molecular weight based on the elution volume of polymer chain. Since hyperbranched polymer tends to be more densely compacted, the conventional GPC underestimates the molecular weight of the polymer. But light scattering GPC calculates the molecular weight based on the light that has been scattered, and has nothing to do with the elution volume. That’s why the absolute molecular weight for hyperbranched polymer is way higher than the relative molecular weight.
Figure 4.6.1 Absolute molecular weight vs. Relative molecular weight for both linear and hyperbranched glycopolymer
CHAPTER V

CONCLUSION AND FUTURE WORK

A truly hyperbranched homo glycopolymer was successfully synthesized. Since the truly hyperbranched glycopolymer is more densely compacted than linear polystyrene, the conventional GPC will always underestimate the molecular weight of the polymer. But light scattering GPC measures the molecular weight based on the structure of the polymer. Therefore in the plot of absolute molecular weight Vs Relative molecular weight, the slope for hyperbranched polymer is much higher than that for the linear one. This indicates that the degree of branching of synthetic hyperbranched polymer is almost 4 times higher than linear polymer.

Since reliable average dn/dc value for these new type of glycopolymer (both linear and hyperbranched) has been obtained, further research can be done by referencing this value for this type of glycopolymer.

In the future, the protected glycopolymer will be deprotected and ELISA (Enzyme-Linked ImmunoSorbent Assay) can be used to analyze the binding affinity between the
protein and the deprotected glycol-polymer. This type of glycopolymer might have a promising future in protein-based drug delivery.
REFERENCES


APPENDIX

Figure A1 shows the GPC data of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator = 40:1:1:1

Figure A1 GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr₂]:[PMDETA]:[AIBN]=40:1:1:1, 110℃, 72h)

Figure A2 shows the GPC data of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator = 50:1:1:1
Figure A2 GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr₂]:[PMDETA]:[AIBN]=50:1:1:1, 110°C, 72h)

Figure A3 shows the GPC data of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 100:1:1:1
Figure A3 GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=100:1:1:1, 110 °C, 72h)

Figure A4 shows the dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 40:1:1:1

Figure A5 shows the dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=40:1:1:1, 110 °C, 72h)

Figure A4 dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=40:1:1:1, 110 °C, 72h)

Figure A5 shows the dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 50:1:1:1
Figure A5 dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr₂]:[PMDETA]:[AIBN]=50:1:1:1, 110°C, 72h)

Figure A6 shows the dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 100:1:1:1
Figure A6 dn/dc value of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=100:1:1:1, 110℃,72h)

Figure A7 shows the light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 40:1:1:1

Figure A7 light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=40:1:1:1, 110℃,72h)

Figure A8 shows the light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 50:1:1:1
Figure A8 light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=50:1:1:1, 110°C, 72h)

Figure A9 shows the light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification, the mole ratio of reactant was monomer: ligand: catalyst: initiator= 100:1:1:1
Figure A9 light scattering GPC of poly(α,β-6-Acrylate-1,2,3,4-tetraacetate mannopyranose) after purification. ([M]:[CuBr$_2$]:[PMDETA]:[AIBN]=100:1:1:1, 110°C, 72h)

Figure A10 shows the GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.

![Auto-Scaled Chromatogram](image)

<table>
<thead>
<tr>
<th>Dist Name</th>
<th>Mn</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz+1</th>
<th>Polydispersity</th>
<th>MW Marker 1</th>
<th>MW Marker 2</th>
</tr>
</thead>
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<td>11550</td>
<td>25190</td>
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<td>1.59555</td>
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</tr>
</tbody>
</table>

Figure A10 GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 60h)

Figure A11 shows the GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.
Figure A11 GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 72h)

Figure A12 shows the GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.
Figure A12 GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr₂]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 84h)

Figure A13 shows the GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.

![Auto-Scaled Chromatogram](image)

**GPC Results**

<table>
<thead>
<tr>
<th>Dist Name</th>
<th>M₀</th>
<th>Mₙ</th>
<th>Mₚ</th>
<th>Mₚ/M₀</th>
<th>Polydispersity</th>
<th>Mₚ/Mₚ Marker 1</th>
<th>Mₚ/Mₚ Marker 2</th>
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<td>2.104188</td>
<td></td>
</tr>
</tbody>
</table>

Figure A13 GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr₂]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 96h)

Figure A14 shows the dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.
Figure A14 dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 60h)

Figure A15 shows the dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.
Figure A15 dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 72h)

Figure A16 shows the dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.

Determine dn/dc from RI

![Graph showing differential refractive index vs concentration](image)

Fit $R^2=0.9995$

Figure A16 dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 84h)

Figure A17 shows the dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.
Figure A17 dn/dc value of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr₂]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 96h)

Figure A18 shows the light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.
Figure A18 light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 60h)

Figure A19 shows the light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.

Figure A19 light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 72h)

Figure A20 shows the light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.
Figure A20 light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 84h)

Figure A21 shows the light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification.

Figure A21 light scattering GPC of poly(2-Bromo-3-acryloyl-(α,β-6-O-1,2,3,4-tetraacetate mannopyranose)) after purification. ([I]:[CuBr$_2$]:[PMDETA]:[AIBN]=10:1:1:0.25, 110°C, 96h)