TRIBLOCK COPOLYMERS OF PLLA-PEG-PLLA FOR NERVE GUIDANCE CHANNEL SCAFFOLDS VIA 3D PRINTING

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By

Wei Wu

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The peripheral nervous system (PNS) is a complicated and extensive network of nerves that are the means by which the brain and spinal cord control the rest of the body. The PNS is fragile and can be easily damaged by injuries or trauma. Surgical treatment is the only remedy available currently, with the gold standard for defects greater than 8 mm being autologous nerve grafts. In addition, nerve grafts have been particularly ineffective at repairing critical-size nerve defects (> 3 cm). Scaffold-based strategies where a tubular nerve guidance channel (NGC) is used to bridge the nerve defect have been promoted as a potential alternative that could avoid the additional surgeries and associated donor site morbidity involved in the harvest of nerve grafts. Current research efforts mainly focused on creating more complex NGCs that can support regeneration of critical-size defects.

My research aims to use additive manufacturing technologies to create tunable NGCs with new biomaterials. The use of biodegradable block copolymers with both hydrophilic and relative hydrophobic functions can provide a flexible, partially-hydrated, biocompatible and bioresorbable NGC shell. In this study, ABA type triblock copolymers of polyethylene glycol (PEG; B block) combined with poly(L-lactic acid) (PLLA; A blocks) were synthesized with varied molecular weights of PEG and different degrees of polymerization of PLLA and were characterized with gel permeation chromatography (GPC), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and
rheometry to determine molecular weight, polymer structure, and thermal and physical properties. In addition, equilibrium water content was evaluated and correlated to polymer structure. Characterization results showed that the copolymers with longer PLLA chains exhibited higher hardness but lower flexibility. The increasing addition of PLLA decreased the melting point, while increasing the PEG molecular weight increased the melting point. Water absorption increased with longer PEG blocks, however this also decreased copolymer integrity. Such degradable thermoplastic elastomers that are amenable to extrusion printing of flexible polymer tubes and exhibit tunable water content hold great promise for further development and application as cellular NGCs for the repair of peripheral nerve defects.
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NOMENCLATURE

\( G' \)  
Storage modulus, MPa

\( \Delta H_m \)  
Heat of melting, J/g

\( m \)  
Mass, g

\( M_n \)  
Number average molecular weight, g/mol

\( M_r \)  
Molecular weight of polymer repeating units, g/mol

\( M_w \)  
Weight average molecular weight, g/mol

\( n \)  
Moles, mol

\( T_{m, \text{onset}} \)  
Onset melting temperature, °C

\( T_{m, \text{peak}} \)  
Peak melting temperature, °C
1.0 INTRODUCTION

Nerve tubes for peripheral nerve repair have been extensively investigated and both natural materials and synthetic materials have been tested experimentally [4]. Meanwhile, 3D printing has been increasingly used in research and medical therapeutics for rational, computer-aided design of biomaterial-based scaffolds with complex architecture. With 3D printing technology, patient specific nerve guidance channels with biodegradable materials that possess required functions and properties can be produced to aid peripheral nerve repairing. Poly (l-lactic) acid (PLLA) as a polyester, has been used to make both industry plastic and medical biopolymers [8]. It is a biodegradable material, and can be made into commercial PLLA filament for 3D printers to produce strong and solid structures. PLLA as a sustainable biomaterial, can be obtained directly from cornstarch or sugar [8]. It is also a safe material that is vastly utilized in toy manufacturing industries. PLA melts around 180°C [10] which is relatively high comparing with other 3D printer filaments such as polycaprolactone (PCL) that melts around 60°C. The hydrolysis, biodegradation and mechanical properties of PLLA highly depend on its molecular weights. A higher molecular weight PLLA can be elongated more but possessed less tensile strength [8]. The application of PLLA homopolymer as an implant is not ideal because it has many drawbacks such as brittleness and hardness [13]. PLLA also has poor compatibility with soft tissues due to its rigidity and hydrophobic properties [13]. Thus, PLLA itself may be a great biomaterial but its mechanical and biological properties may not be suitable for nerve guidance channels which require some degree of flexibility and tissue compatibility.
Researcher have found that polyethylene glycol (PEG) hydrophilic segment can be introduced onto PLLA hydrophobic chain to control hydrophilicity and degradability to accomplish different purposes such as drug delivery or implants [16]. PEG is soluble in water and it is a nontoxic material that is approved by U.S. Food and Drug Administration for the use in human body [11]. Incorporating soft PEG segment onto hard PLLA chain can manipulate the mechanical properties of PLLA and increase water absorption and tissue compatibility. Many copolymers containing PLLA and PEG segments have been synthesized including PLLA-PEG-PLLA, mPEG-PLLA and PEG-PLLA-PEG [6].

A triblock or multiblock copolymers containing soft and hard segments can prevent plastic deformation and form thermoplastic elastomers (TPEs) with rubbery elasticity [13]. PLLA-PEG-PLLA, in particular, has soft segment in the middle and hard domains at both ends which can form phase separation at lower temperature. The PLLA domains crosslinked where the PEG domains stay soft, which allows the material to be soft but flexible. In addition, an ABA type triblock copolymer with hydrophilic B center is capable of swelling water rapidly that forms a biodegradable, cross-linked hydrogel [9]. A hydrogel system can absorb a lot of water while maintaining its 3D structure [2]. The PEG portion in PLLA-PEG-PLLA triblock copolymer can increase water absorption by 80% with only 50 mole% PEG [12]. With a controlled PEG portion in the triblock copolymer system, a partially hydrated material can be fabricated with a higher biocompatibility than PLLA homopolymer. Furthermore, the addition of hydrophilic and non-biodegradable PEG can improve degradation pattern of polyesters since it absorbs a lot water within the copolymers [9].
Currently, researchers have found many pathways to copolymerize PLLA and PEG. The PLLA-PEG copolymers are synthesized by ring-open polymerization (ROP) and initiated by PEG [16]. The PLLA is initiated by the hydroxyl ending group on PEG chains. Regular PEG has two hydroxyl groups at both ends which will produce a triblock copolymer after ROP. Monohydroxy-PEG with only one hydroxyl group is used to make mPEG-PLLA diblock copolymer. As an initiator, the ratio of PEG in the reaction can be manipulated to control the degree of polymerization of PLLA. Higher molecular weight diblock copolymers of mPEG-PLLA were produced with lower concentration of mPEG macroinitiator [16]. Many researchers have found stannous octoate (Sn(Oct)2) a suitable catalyst for ROP of PLLA onto PEG initiator. The ROP of PLLA will produce water as a byproduct, thus reaction is usually carried out above water boiling temperature for the reaction to proceed forward. He et. al., prepared PEG-PLA diblock copolymer using ring-open polymerization process at 120°C for 12 hours [6]. Other processes for the synthesis of PLLA-PEG-PLLA include heating at 120°C for 48 hours using polymerization tube [11] and using microwave irradiation at 100°C for 10-30 mins [16].

In our study, ABA type triblock copolymers of polyethylene glycol (PEG; B block) combined with poly(l-lactic acid) (PLLA; A blocks) were synthesized with varied molecular weights of PEG (M_n = 1450, 3400 and 8000) and different degrees of polymerization of PLLA and characterized with gel permeation chromatography (GPC), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR) and rheometry to determine molecular weight, polymer structure, and thermal and physical properties.
2.0 CRITICAL LITERATURE REVIEW

2.1 3D Printing of Biomaterials

Additive manufacturing, also known as 3D printing, has become a tool for the fabrication of complex architecture through computer-aided design. The 3D printing of biomaterials involves the physical extrusion of biomaterials that solidifies upon deposition and the layer by layer construction of specific scaffolds that is aiming at biological interactions [7]. The two most important aspects of the scaffolds using 3D printing technology are biomaterials and structure. As shown in Figure 1, the biomaterials used for 3D printing should be biocompatible, and extrudable in a laminar fashion while maintaining its structure after printing.

Figure 1: Ink requirements for 3D biomaterial printing [7].

PLLA is a biodegradable material for 3D printing applications. Almeida et al. explored the effect of different 3D structure on inflammation using PLA based material and the results showed that both the surface properties and geometry of the scaffold can affect the monocyte/macrophage responses where the macrophage morphology are mostly affected by material properties but slightly affected by the scaffold structure [1].
2.2 Nerve Guidance Channels

The traditional way of repairing nerve defects without stretching the nerve ends is autologous nerve graft (Figure 2; A) with sural nerve taken from the patients. The disadvantages of this kind of treatment are obvious where extra incisions are required and the nerve size of the damaged nerve and the donor nerve does not exact match each other. A nerve tube (Figure 2; B) with right-off-the-shelf availability in different sizes can be used to repair nerve injuries allowing the regeneration of nerve cells.

![Figure 2: (A) Repair of a nerve injuries with autologous sural nerve grafts; (B) Nerve tube repair [4].](image)

2.2.1 Physical Characteristics of the Nerve Tube

The generation of fibrin matrix (Figure 3) within the nerve tubes is the key element for the regeneration of nerve cells. The dimensions of the nerve tube including the ability of prefilling nutrients or porosity are both able to help the formation of fibrin matrixes.
The permeability of the nerve tube is another critical dimension for cells or other molecules that are involved in the formation of fibrin matrixes to enter [4]. The permeability could be affected by both pore size or hydrophilicity of the nerve tube material. In addition, many other physical properties including swelling and degradation may negatively affect the regenerating nerve by decreasing the tensile properties or creating toxic or acidic degradation products. With porosity and permeability, a nerve tube should also be strong enough to hold its structure, biocompatible and non-toxic.

2.2.2 Clinical Use

Various nerve tubes are currently used in clinical trials including Neurotube (PGA), Neuragen (collagen), Neurolac (polycaprolactone), Neuro-Matrix and Neuroflex (both collagen), and SalaBridge (Hydrogel, nonbiodegradable) [4]. These nerve tubes are mainly used for small gaps (<3 cm) nerve regeneration. However, the growth accuracy of the regeneration across the nerve tubes as well as the long-term effects of biodegradable

Figure 3: The different phases of regeneration across the nerve tube [4].
nerve tubes has not yet been characterized extensively. Cautions should still be taken using nerve tubes for peripheral nerve repair.

2.3 Thermoplastic Elastomers and Triblock Copolymers

2.3.1 Thermoplastic Elastomers

The interest in biodegradable polymers in clinical use grows and the mechanical properties of the implants that mimic the host tissue are of great importance. The vast majority of the biodegradable polymers have their limits in extendibility [3]. Using thermoplastic elastomers (TPEs) from copolymers can increase the extendibility of the biodegradable materials. TPEs are materials that possess elastic property at low temperature but melts at higher temperature just like thermoplastics. It can be recycled and remodeled which provides opportunities to fabricate on demand scaffolds for specific patients. TPEs are usually triblock or multiblock copolymers consisting flexible soft segments and hard segments that prevents the plastic deformation [13]. ABA linear copolymers where A segments and B segments are not miscible and segregate in phase-separated domains can create physical cross-links that result in the elastic property [5]. PLA can be used as the hard segment to create partial degradability for the TPEs. Many PLA-block-S-block-PLA (S = soft segment) have been studied including aliphatic polyesters, polycarbonate, polyether and polyisoprene ect. [14]. The TPEs with biodegradable A segments and soft B segment could provide flexible and biodegradable properties for nerve guidance channels.

2.3.2 PLLA-PEG-PLLA Triblock Copolymers

The PLLA-PEG-PLLA triblock copolymers have attracted the attentions of material scientists with interests in implants and drug delivery systems. ABA type
triblock copolymers with hard A segments of PLA and soft B segments of PEG are classified due to its structure. The copolymers with different structures are shown in Figure 4.

![Figure 4: Architectures of block copolymers [9].](image)

He et al. synthesized both PLA-PEG-PLA and PEG-PLA-PEG triblock copolymers to study the drug release properties. The ABA type copolymer PLA-PEG-PLA was synthesized using PEG and lactide where the BAB type copolymer PEG-PLA-PEG was prepared by first synthesizing mPEG-PLA diblock copolymer and then reacted with hexamethylene diisocyanate (HMDI) [6].

Harrane et al. also created PLA-based biodegradable and tunable soft elastomers with long PEG center. The material possesses certain degree of elasticity but their hydrogels that containing high degree of polymerization (100-200) of PEG blocks and short PLA blocks (DP = 3) are not able to recover its shape [5].
Cohn and Hotovy-Solomon reported their work of multiblock PEO/PLA thermoplastic elastomers (Figure 5) with the synthesis of their PEO/PLA (PELA) copolymers and chain extension with hexamethylene diisocyanate (HDI) [3].

![Figure 5: Schematic and structure of PELA copolymers [3].](image)

The water absorption of PLLA-PEG-PLLA with long center PEG chain was studied by Mohammadi-Rovshandeh et al. showing a huge impact of water absorption with respect to PEG mole percent in block copolymers in Figure 6 [11].

![Figure 6: Water absorption versus PEG mole percent [11].](image)

The water absorption is one of the functions that affects the degradation of PLA within the copolymers. As shown in the figure below, the PLA phase has a partially crystalline center and an amorphous rubbery shell at swollen state [9].
Kissel et al. also reported that PLLA-PEG-PLLA with PEG 35000 center block has good biocompatibility and superior cytotoxicity properties than copolymers with PEG 3000 center block [9]. Many scientists have researched the potential use of PLLA-PEG-PLLA TPEs as implant materials due to their mechanical properties, water absorptivity and biodegradability. PLLA-PEG-PLLA as an extrudable thermoplastic elastomer, its water absorptivity can affect its biocompatibility and provide tunable biodegradability.
3.0 EXPERIMENTAL

3.1 Materials

Pharmaceutical grade PEGs (Mn=1450, 3400, 8000) were purchased from Polysciences, Inc. L-lactide (3,6-Dimethyl-1,4-dioxane-2,5-dione) and stannous octoate (Tin(II) 2-ethylhexanoate) were purchased from Sigma-Aldrich. L-lactide was stored in refrigerator with temperature between 2 to 8°C to prevent self-polymerization. HPLC grade toluene was dried using molecular sieves a few days before experiments. HPLC grade water and methanol were purchased from Fisher Scientific and filtered with Millipore 0.22 µm filter. The solvents were mixed with volume fractions of 80% methanol and 20% water as the mobile phase for GPC.

3.2 Synthesis

1.250 g of PEG was added into a 500 mL three-neck round-bottom flask and 12.5 mL of dried toluene was introduced to the flask using glass pipet to dissolve the PEG. The system was pre-dried under vacuum until all the volatiles were fully removed. Dried PEG was then dissolved with 12.5 mL of toluene followed by 0.890 g of l-lactide and 8.9 mL of toluene. The toluene was added into the flask based on the ratio of 10 ml per gram of solid. Stannous octoate was pipetted into the flask at a mass fraction of 20% of the total amount of PEG and l-lactide. The concentration of l-lactide was controlled to obtain different PLLA loading on PEG chains. For relative lower and higher PLLA loading copolymer, 0.445 g and 1.780 g of l-lactide was added respectively. The mixture was then heated up to 140°C in oil bath and allowed reflux for 14h. The system was pulled vacuum for one minute and then filled with nitrogen. This process was repeated three times to ensure all the oxygen was removed from the system. Schlenk line was used to regulate
the nitrogen and vacuum line that were connected to the system. The synthesis was
carried out with ROP under nitrogen atmosphere. After the synthesis, the system was
allowed several hours to cool down and the product was then dried using a rotary
evaporator to remove all the solvents. The dried product was dissolved in
dichloromethane (CH₂Cl₂) and precipitated in cold diethyl ether. The filtered copolymers
were collected in scintillation vials and dried at room temperature in vacuum oven for at
least 24h. All dried copolymers were ground into powders prior to analytics and further
experiments.

3.3 Characterizations

1H NMR (500 MHz) was used to identify the polymer structure and quantify the
hydrogen content of copolymers. All samples were dissolved in deuterated chloroform
(CDCl₃) with a concentration of 20 mg/ml. The pure PEG samples were also analyzed to
obtain a direct comparison of the peak locations as well as intensities.

TOSOH EcoSEC HLC-8320 GPC was used to determine the detailed molecular
weight information of copolymers. The number average molecular weight (Mₙ), weight
average molecular weight (M_w), as well as polydispersity indexes were measured three
times for each copolymer. The solubility of copolymers in the GPC mobile phase
containing 80% methanol and 20% water was tested prior to analysis. The flow rate of
the mobile phase was 0.5 mL/min for both sample and reference column, and the
calibration curve was carried out using PEG standards with molecular weights of 150-
69190 g/mol.

DSC results were obtained by using TA Q2000. All copolymer samples were
prepared three times in sealed DSC aluminum pans with lids. The range of the sample
mass were from 20 mg to 40 mg. The analyzing process was carried out with a heating rate of 10°C/min from 0°C to 100°C, and ramping down with a cooling rate of 10°C/min from 100°C to 0°C followed by a ramping up with a heating rate of 5°C/min from 0°C to 100°C. The last heating thermogram was obtained for analysis.

A rheometer (TA Discovery HR-1) was used to test the mechanical properties of the copolymer in both solid and melted form. The lost and storage moduli were measured upon cooling at different temperatures. For storage modulus test, copolymers were tested with a starting temperature of 100°C and ramped down with a rate of 10°C/min to 0°C. The copolymers were soaked at starting temperature for 2 min before cooling to ensure all copolymers were melted.
4.0 RESULTS AND DISCUSSION

We synthesized copolymers for the use in nerve regeneration and characterized their biophysical and chemical characteristics. The synthesized copolymers are white and opaque. The copolymers using PEG 1450 are sticky and pasty, and copolymers using PEG 3400 and 8000 center chains were in the forms of white powder after grinding. From lower molecular weight to higher molecular weight, copolymers were becoming increasingly stronger and the copolymer morphology turned from a more flexible pasty state to a tougher waxy state. For copolymers using the same PEG center block, higher loading copolymers were easier to grind into finer powders. The materials can be easily melted and extruded into hard structures. The extruded object can swell a lot of water but retaining its integrity in water for days as shown in Figure 8.

![Figure 8: Water swelling test of extruded object in (A) the same day; (B) 3 days.](image)

Figure 8: Water swelling test of extruded object in (A) the same day; (B) 3 days.
The extruded object was cut into a stick to test its flexibility manually. As shown in the following figure, the material possessed some flexibility but breaks if bended above 90 degrees. This preliminary bending test showed that the material is hard and flexible and matched the characteristics of TPEs.

In detailed characterizations were conducted on molecular weight, structure and physical behavior of the copolymers.

### 4.1 $^1$H NMR

The NMR spectrum shows PLLA-PEG-PLLA triblock copolymers have three intense peaks that represent three different protons. As shown in Figure 10, PLLA has two types of protons and PEG has one type of proton. Peaks of the copolymer sample appear at 5.2 ppm (-CH-), 4.3 ppm (-CH-), 3.6 ppm (-CH$_2$-CH$_2$-O-) and 1.5 ppm (-CH$_3$) and the ratios of protons were calculated to obtain the molecular weight of PLLA that were added onto PEG. The shifting of the peaks at 4.3 ppm could be the hydrogen from -CH- at the connection point of PEG and PLLA where the surrounding groups were slightly different from the other -CH- groups. The addition of PLLA were calculated directly from the ratios of -CH- and -CH$_2$-CH$_2$-O- from each block. PEG molecular weight were assumed to be the same as what they are labeled. As an example, the
molecular weight of PEG 3400 with high PLLA loading were calculated using the following equation:

\[ M_n = M_{PEG} + DP_{PLLA} \times M_r_{PLLA} = 3400 + \frac{1.16/4}{9.09/4} \times \frac{3400 - 18}{44} \times 144 = 4812 \]

Table 1 summarizes the all the spectra results from \(^1\)H NMR.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Copolymers</th>
<th>(M_n) (g/mol)</th>
<th>(M_n)(_{PLLA}) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PEG(_{13})</td>
<td>1450</td>
<td>-</td>
</tr>
<tr>
<td>A1</td>
<td>PLLA(<em>{0.9})(</em>{-})PEG(<em>{33})(</em>{-})PLLA(_{0.9})</td>
<td>1711</td>
<td>261</td>
</tr>
<tr>
<td>A2</td>
<td>PLLA(<em>{1.1})(</em>{-})PEG(<em>{33})(</em>{-})PLLA(_{1.5})</td>
<td>1877</td>
<td>427</td>
</tr>
<tr>
<td>A3</td>
<td>PLLA(<em>{3.2})(</em>{-})PEG(<em>{33})(</em>{-})PLLA(_{3.2})</td>
<td>2380</td>
<td>930</td>
</tr>
<tr>
<td>B</td>
<td>PEG(_{79})</td>
<td>3400</td>
<td>-</td>
</tr>
<tr>
<td>B1</td>
<td>PLLA(<em>{1.9})(</em>{-})PEG(<em>{77})(</em>{-})PLLA(_{1.9})</td>
<td>3937</td>
<td>537</td>
</tr>
<tr>
<td>B2</td>
<td>PLLA(<em>{2.7})(</em>{-})PEG(<em>{77})(</em>{-})PLLA(_{2.7})</td>
<td>4179</td>
<td>779</td>
</tr>
<tr>
<td>B3</td>
<td>PLLA(<em>{4.9})(</em>{-})PEG(<em>{77})(</em>{-})PLLA(_{4.9})</td>
<td>4812</td>
<td>1411</td>
</tr>
<tr>
<td>C</td>
<td>PEG(_{182})</td>
<td>8000</td>
<td>-</td>
</tr>
<tr>
<td>C1</td>
<td>PLLA(<em>{2.6})(</em>{-})PEG(<em>{182})(</em>{-})PLLA(_{2.6})</td>
<td>8747</td>
<td>747</td>
</tr>
<tr>
<td>C2</td>
<td>PLLA(<em>{4.2})(</em>{-})PEG(<em>{182})(</em>{-})PLLA(_{4.2})</td>
<td>9196</td>
<td>1196</td>
</tr>
<tr>
<td>C3</td>
<td>PLLA(<em>{10.1})(</em>{-})PEG(<em>{182})(</em>{-})PLLA(_{10.1})</td>
<td>19012</td>
<td>2912</td>
</tr>
</tbody>
</table>

**Figure 10:** (A) Structure of PLLA-PEG-PLLA triblock copolymers; (B) \(^1\)H NMR spectrum of pure PEG 3400; (C) \(^1\)H NMR spectrum of PEG 3400 with high PLLA loadings.
4.2 GPC

The GPC analysis of the synthesized copolymers supported the $^1$H NMR results which gave the evidence of the molecular weight changes for different PLLA loadings of the copolymers. The detailed information for synthesized PLLA-PEG-PLLA copolymers is shown in Table 2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Copolymers</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w/M_n$ (PDI)</th>
<th>Molar ratio (PEG/PLLA)</th>
<th>Mass ratio (PEG/PLLA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PEG$_{33}$</td>
<td>1451 ± 2.2</td>
<td>1.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A1</td>
<td>PLLA$<em>{1.2}$-PEG$</em>{33}$-PLLA$_{1.2}$</td>
<td>1788 ± 2.9</td>
<td>1.09</td>
<td>14.1</td>
<td>4.3</td>
</tr>
<tr>
<td>A2</td>
<td>PLLA$<em>{1.9}$-PEG$</em>{33}$-PLLA$_{1.9}$</td>
<td>1997 ± 0.5</td>
<td>1.07</td>
<td>8.7</td>
<td>2.7</td>
</tr>
<tr>
<td>A3</td>
<td>PLLA$<em>{3.8}$-PEG$</em>{33}$-PLLA$_{3.8}$</td>
<td>2547 ± 1.7</td>
<td>1.11</td>
<td>4.3</td>
<td>1.3</td>
</tr>
<tr>
<td>B</td>
<td>PEG$_{71}$</td>
<td>3137 ± 0.5</td>
<td>1.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B1</td>
<td>PLLA$<em>{1.2}$-PEG$</em>{71}$-PLLA$_{1.2}$</td>
<td>3494 ± 7.9</td>
<td>1.07</td>
<td>28.7</td>
<td>8.8</td>
</tr>
<tr>
<td>B2</td>
<td>PLLA$<em>{3.1}$-PEG$</em>{71}$-PLLA$_{3.1}$</td>
<td>4029 ± 1.9</td>
<td>1.09</td>
<td>11.5</td>
<td>3.5</td>
</tr>
<tr>
<td>B3</td>
<td>PLLA$<em>{5.2}$-PEG$</em>{71}$-PLLA$_{5.2}$</td>
<td>4633 ± 11.0</td>
<td>1.07</td>
<td>6.9</td>
<td>2.1</td>
</tr>
<tr>
<td>C</td>
<td>PEG$_{193}$</td>
<td>8482 ± 76.4</td>
<td>1.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C1</td>
<td>PLLA$<em>{2.6}$-PEG$</em>{193}$-PLLA$_{2.6}$</td>
<td>9240 ± 47.3</td>
<td>1.08</td>
<td>36.6</td>
<td>11.2</td>
</tr>
<tr>
<td>C2</td>
<td>PLLA$<em>{3.3}$-PEG$</em>{193}$-PLLA$_{5.3}$</td>
<td>10022 ± 30.4</td>
<td>1.09</td>
<td>18.0</td>
<td>5.5</td>
</tr>
<tr>
<td>C3</td>
<td>PLLA$<em>{8.3}$-PEG$</em>{193}$-PLLA$_{8.3}$</td>
<td>10858 ± 59.4</td>
<td>1.15</td>
<td>11.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The molecular weights of copolymers increased from sample 1 to 3 as more PLLA were added to the formula using the same PEG initiator amount. The addition of PLLA ranged from 337 to 2376 g/mol and the degree of polymerization (DP) of PLLA ranged from 2.4 to 16.6 on each side of the PEG. The polydispersity (PDI) of the copolymers ranged from 1.07 to 1.15 showing a high uniformity in the molecular weight distribution. The degree of polymerization for each copolymer was obtained using the following equation:

$$DP_{PEG} = \frac{M_n}{M_r^{PEG}}$$

$$DP_{PLLA} = \frac{M_n - M_n^{PEG}}{M_r^{PLLA}}$$

Where the $M_r^{PLLA}$ that represents the molecular weight of PLLA repeating units equals to 144, and $M_r^{PEG}$ is 44. PEG has two hydroxyl group on both ends of the polymer
backbone so PLLA has equal opportunity to add on each side of the PEG center chain. The degree of polymerization of PLLA was divided by two indicating the PLLA were equally added onto both sides of the PEG. The PDI that demonstrates the range of the polymer molecular weight distribution was obtained from GPC directly. The molar and mass ratio of PEG to PLLA was calculated using the following equations:

\[
\text{Molar Ratio } \frac{\text{PEG}}{\text{PLLA}} = \frac{n_{\text{PEG}}}{n_{\text{PLA}}} = \frac{M_n_{\text{PEG}}}{M_r_{\text{PEG}}} \frac{M_n_{\text{PLA}}}{M_r_{\text{PLA}}}
\]

\[
\text{Mass Ratio } \frac{\text{PEG}}{\text{PLLA}} = \frac{m_{\text{PEG}}}{m_{\text{PLA}}} = \frac{M_n}{M_n - M_n_{\text{PEG}}}
\]

The mass ratio of PEG to PLLA ranges from 1.3 to 11.2 and the molar ratios of PEG to PLLA ranges from 4.3 to 36.6. Lower ratios indicated a higher PLLA contents in the copolymers. This resulted in a PEG mole percent of 81.11% to 97.08%. The pure PEG molecular weight out of the box was also analyzed using GPC to confirm the molecular weight. As shown in Table 2, the PEG 3400 has a molecular weight around 3137 which is lower than labeled. PEG 8000 has a relative higher molecular weight of 8482 than what it is labeled. As the molecular weight of PEG increases, the PLLA degree of polymerization on the copolymer gets longer as well. This is reasonable considering the same amount of PEG and PLLA were added to the flask for each low, medium and high loading formulas. Using same amount of PEG, the higher molecular weight PEG contains fewer numbers of molecules. The ROP was initiated by PEG, thus fewer initiators would result in longer PLLA chains. The GPC calibration curve was created using PEG which best represents the changes among the samples.
The chromatography plots in Figure 11 demonstrate a clear trend of the peaks shifting to a lower retention time as more PLLA was added onto PEG center block. The copolymers for each PEG was categorized into low loadings (LL), medium loadings (ML) and high loadings (HL) with respect to different PLLA degree of polymerization for each group of samples.

![Figure 11: GPC spectra for different groups of copolymers with various PLLA loadings. (A) PEG 1450 center block copolymers; (B) PEG 3400 center block copolymers; (C) PEG 8000 center block copolymers.](image)

The poly dispersity increases respectively with the increment of PLLA loadings and the molecular weights which can be observed from Figure 11 that the distribution of the copolymer retention time gets broader. However, all the copolymers are monodispersed because they all have only one peak on the spectra.

### 4.3 DSC

The DSC results showed the thermal properties of the copolymers. In particular with the biomaterials, DSC data provides the basis for the selection of potential viable materials for implants. The material that has onset melting temperature higher than body temperature would be ideal for the use as implantable scaffold. The peak melting temperature is the key element of finding the right temperature for 3D printing using extrusion method. The heat of melting indicated the amount of heat per grams of material that is required to melt the copolymer. A summary for all DSC results for the synthesized
copolymers is shown in Table 3 where all copolymers were tested 3 times to assess reproducibility and the ramping temperature was kept at 5°C/min from 0°C to 100°C.

Table 3: Detailed DSC results of synthesized copolymers

<table>
<thead>
<tr>
<th>Groups</th>
<th>Copolymers</th>
<th>$T_{m, \text{onset}}$ (°C)</th>
<th>$T_{m, \text{peak}}$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PEG&lt;sub&gt;33&lt;/sub&gt;</td>
<td>37.63 ± 0.51</td>
<td>51.56 ± 1.85</td>
<td>122.43 ± 0.52</td>
</tr>
<tr>
<td>A1</td>
<td>PLLA&lt;sub&gt;1.2&lt;/sub&gt;-PEG&lt;sub&gt;33&lt;/sub&gt;-PLLA&lt;sub&gt;1.2&lt;/sub&gt;</td>
<td>24.81 ± 0.75</td>
<td>36.65 ± 0.24</td>
<td>63.83 ± 1.59</td>
</tr>
<tr>
<td>A2</td>
<td>PLLA&lt;sub&gt;1.9&lt;/sub&gt;-PEG&lt;sub&gt;33&lt;/sub&gt;-PLLA&lt;sub&gt;1.9&lt;/sub&gt;</td>
<td>20.63 ± 0.47</td>
<td>32.42 ± 0.26</td>
<td>47.41 ± 1.88</td>
</tr>
<tr>
<td>A3</td>
<td>PLLA&lt;sub&gt;3.8&lt;/sub&gt;-PEG&lt;sub&gt;33&lt;/sub&gt;-PLLA&lt;sub&gt;3.8&lt;/sub&gt;</td>
<td>13.20 ± 0.23</td>
<td>24.32 ± 0.77</td>
<td>24.78 ± 0.71</td>
</tr>
<tr>
<td>B</td>
<td>PEG&lt;sub&gt;71&lt;/sub&gt;</td>
<td>53.69 ± 0.20</td>
<td>61.75 ± 0.44</td>
<td>136.07 ± 1.09</td>
</tr>
<tr>
<td>B1</td>
<td>PLLA&lt;sub&gt;1.2&lt;/sub&gt;-PEG&lt;sub&gt;71&lt;/sub&gt;-PLLA&lt;sub&gt;1.2&lt;/sub&gt;</td>
<td>40.23 ± 0.49</td>
<td>46.14 ± 0.28</td>
<td>74.41 ± 0.38</td>
</tr>
<tr>
<td>B2</td>
<td>PLLA&lt;sub&gt;3.1&lt;/sub&gt;-PEG&lt;sub&gt;71&lt;/sub&gt;-PLLA&lt;sub&gt;3.1&lt;/sub&gt;</td>
<td>37.29 ± 1.21</td>
<td>44.53 ± 0.46</td>
<td>65.67 ± 1.15</td>
</tr>
<tr>
<td>B3</td>
<td>PLLA&lt;sub&gt;5.2&lt;/sub&gt;-PEG&lt;sub&gt;71&lt;/sub&gt;-PLLA&lt;sub&gt;5.2&lt;/sub&gt;</td>
<td>33.58 ± 0.07</td>
<td>41.26 ± 0.14</td>
<td>42.65 ± 1.14</td>
</tr>
<tr>
<td>C</td>
<td>PEG&lt;sub&gt;193&lt;/sub&gt;</td>
<td>58.57 ± 0.02</td>
<td>66.24 ± 0.09</td>
<td>148.03 ± 2.42</td>
</tr>
<tr>
<td>C1</td>
<td>PLLA&lt;sub&gt;2.6&lt;/sub&gt;-PEG&lt;sub&gt;193&lt;/sub&gt;-PLLA&lt;sub&gt;2.6&lt;/sub&gt;</td>
<td>49.60 ± 0.33</td>
<td>56.37 ± 0.31</td>
<td>93.18 ± 2.45</td>
</tr>
<tr>
<td>C2</td>
<td>PLLA&lt;sub&gt;3.3&lt;/sub&gt;-PEG&lt;sub&gt;193&lt;/sub&gt;-PLLA&lt;sub&gt;3.3&lt;/sub&gt;</td>
<td>47.21 ± 0.25</td>
<td>54.09 ± 0.14</td>
<td>75.20 ± 1.37</td>
</tr>
<tr>
<td>C3</td>
<td>PLLA&lt;sub&gt;8.3&lt;/sub&gt;-PEG&lt;sub&gt;193&lt;/sub&gt;-PLLA&lt;sub&gt;8.3&lt;/sub&gt;</td>
<td>43.30 ± 0.35</td>
<td>51.33 ± 0.39</td>
<td>57.49 ± 1.78</td>
</tr>
</tbody>
</table>

* results obtained from GPC

According to Krzysztof Pielichowski and Kinga Flejtuch’s study on pure PEG with DSC, the melting peak stays relatively the same when the heating rate is 5°C/min or lower [15]. All samples were ramped to 200°C only once, however none of them showed an endothermic peak above 100°C indicating no PLLA homopolymer or water was mixed with the synthesized copolymers. Interestingly, PLLA melted around 180°C but no peak was detected above 100°C. This means the block copolymer only showed a unique and PEG-related melting temperature. As a copolymer, this works better if compared with diblock copolymers of mPEG-PLLA since it only has one melting temperature. According to Zhou et al., diblock copolymers of mPEG-PLLA have two melting temperature peaks for each PEG and PLLA blocks [17]. The triblock copolymers of PLLA-PEG-PLLA with only one melting temperature are great materials for 3D printing since an accurate melting temperature can be identified and controlled to ensure the printing materials completely melt before extruding. Also, PEG has a relative lower melting temperature than PLLA, the copolymer can be kept at relative lower temperature.
melting condition, this provides a better condition for further application including printing with other biological supplements that degrades or deforms at higher temperature.

The three repeating results for each copolymer were consistent. All copolymers showed only one peak representing their melting temperatures. PEG melting temperature increased as its molecular weight increased. Higher molecular weight PEGs had higher interconnections of the chains inside the polymer and it took more energy to melt them.

![Graph showing onset melting temperature of different groups of copolymers](image)

**Figure 12:** Onset melting temperature of different groups of copolymers with various PLLA loadings. (A) PEG 1450 center block copolymers; (B) PEG 3400 center block copolymers; (C) PEG 8000 center block copolymers.

The onset melting temperature indicated the temperature where a material begins to melt. A material with an onset melting temperature lower than 37°C will start to melt once it contacts human body. As shown in Figure 12, the copolymers for PEG 1450 all lies below 37°C which makes them not good materials for implants. However,
copolymers from PEG 3400 or higher has the potential to make implants because some of their onset melting temperatures are higher than 37°C.

![Figure 13: Peak melting temperature of different groups of copolymers with various PLLA loadings. (A) PEG 1450 center block copolymers; (B) PEG 3400 center block copolymers; (C) PEG 8000 center block copolymers.](image)

Peak melting temperature is a key element for the application of 3D printing. The 3D printer can be adjusted to a temperature higher than the peak melting temperature to ensure all the copolymers are melted. With our material, a relative low melting peak allows the extruder to be heated at a lower temperature which is much safer and easier to control.
As shown in Figure 15, a clear trend of melting peak shifting to lower temperatures can be captured as more PLLA was added onto the PEG block. Generally, the PEG degree of crystallinity increases with the increment of its molecular weights [15], however, the presence of PLLA decreases the crystallinity of the copolymer and it
requires less energy for the material to melt. This can also be proved in Figure 14 where the melting enthalpy also decreased with the presence of PLLA. In this experiment, the PEG 1450 copolymers were excluded from further research since both their onset and peak melting temperature are below 37°C which are not practical to make implantable scaffold.

4.4 Rheometry

The rheometer data are summarized in Table 4 showing the crystallization temperature of the synthesized copolymers at various formulas.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Copolymers&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Solidifying Poing (°C)</th>
<th>$G'_\text{max}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>PLLA&lt;sub&gt;1.2&lt;/sub&gt;-PEG&lt;sub&gt;7.1&lt;/sub&gt;-PLLA&lt;sub&gt;1.2&lt;/sub&gt;</td>
<td>31.32 ± 1.47</td>
<td>1.57</td>
</tr>
<tr>
<td>B2</td>
<td>PLLA&lt;sub&gt;3.1&lt;/sub&gt;-PEG&lt;sub&gt;7.1&lt;/sub&gt;-PLLA&lt;sub&gt;3.1&lt;/sub&gt;</td>
<td>30.92 ± 0.66</td>
<td>1.44</td>
</tr>
<tr>
<td>B3</td>
<td>PLLA&lt;sub&gt;5.2&lt;/sub&gt;-PEG&lt;sub&gt;7.1&lt;/sub&gt;-PLLA&lt;sub&gt;5.2&lt;/sub&gt;</td>
<td>19.24 ± 1.27</td>
<td>1.16</td>
</tr>
<tr>
<td>C1</td>
<td>PLLA&lt;sub&gt;2.6&lt;/sub&gt;-PEG&lt;sub&gt;193&lt;/sub&gt;-PLLA&lt;sub&gt;2.6&lt;/sub&gt;</td>
<td>39.15 ± 0.94</td>
<td>1.47</td>
</tr>
<tr>
<td>C2</td>
<td>PLLA&lt;sub&gt;5.3&lt;/sub&gt;-PEG&lt;sub&gt;193&lt;/sub&gt;-PLLA&lt;sub&gt;5.3&lt;/sub&gt;</td>
<td>40.78 ± 3.02</td>
<td>1.21</td>
</tr>
<tr>
<td>C3</td>
<td>PLLA&lt;sub&gt;8.3&lt;/sub&gt;-PEG&lt;sub&gt;193&lt;/sub&gt;-PLLA&lt;sub&gt;8.3&lt;/sub&gt;</td>
<td>31.30 ± 0.75</td>
<td>1.44</td>
</tr>
</tbody>
</table>

<sup>a</sup> results obtained from GPC

The general trend indicated that more PLLA on the PEG chain would result in a lower solidifying point which match the DSC results. With the information of solidifying temperature, the temperature condition for the material after 3D printing can be developed. The extruding temperature could be set up to a few degrees higher than the melting peaks and the printing station could be kept at a relative lower temperature to ensure the material solidifies after printing.
The storage modulus of the copolymers gradually increases as the temperature gradually reaches the crystallization point and sharp increase to the maximum point. This means the material stores some energy when torque was applied and may be elastic in the solid state. As shown in figure 16, all synthesized copolymers have relatively the same maximum storage modulus.

Figure 16: Storage modulus of (A) PEG 3400; (B) PEG 8000 copolymers with different PLLA loadings cooling from 100°C to complete solidify.
5.0 CONCLUSION

The molecular weights and structure of the synthesized copolymers were determined synthesized by GPC and NMR. PLLA-PEG-PLLA with various ratios of PLLA hydrophobic blocks were synthesized during the study and the PLLA degree of polymerization can be controlled by varying the monomer concentration in the reaction mixture. The synthesizing time was reduced to 14 hours using 20 wt% catalyst. The thermal responses of the copolymers were characterized with DSC as well as rheometry. PLLA-PEG-PLLA is a great thermoplastic material which flows above its melting temperature and solidifies below crystallization point. The synthesized copolymers with low molecular weight PEG (Mn = 1450) center block melts at temperatures lower than body temperature which was not ideal for implant materials. Copolymers with PEG (Mn = 3400, 8000) center block have melting temperatures higher than body temperature. The presence of PLLA had a strong influence on the melting temperature and the melting enthalpy of the copolymers. Overall, the increment of PEG molecular weight would increase the melting temperature of the copolymers but the addition of PLLA block decreases the melting temperature. The synthesized copolymers show only one PEG-related melting peak on DSC thermogram unlike deblock copolymers of mPEG-PLLA which have two melting peaks. The temperature difference of the endothermic melting peak and the crystallization temperature obtained from rheometry are within 13°C which gives information of melting and cooling conditions for the extrusion based 3D printing process. The materials have maximum storage modulus of around 1 to 1.5 MPa which means the materials can be elastic and store some energy if torque was applied
6.0 RECOMMENDATION

6.1 Water absorption

The synthesis of the copolymer is successful that different degrees of polymerization of PLLA were introduced onto PEG center block. In our study, the ratio of PEG/PLLA in the pre-reaction is relatively high that all the copolymer synthesized have longer PEG center block than the PLLA block. The water absorption rate of such long center block is high according to Mohammadi-Rovshandeh et al. In order to have a lower water absorption rate of the material, a much longer PLLA block should be added onto the copolymers. Since the PEG is the initiator for the ROP of PLLA, reducing the PEG concentration in the pre-reaction mixture is an approach to achieve longer PLLA blocks. All the synthesized PLLA-PEG-PLLA copolymers have PEG molar ratios higher than 81%. A series of copolymers with PEG molar ratios less than 50% can be synthesized using the same formula but with lower concentration of PEG and higher PLLA concentration.

6.2 Thermal responses

The melting temperature of copolymers is highly influenced by the PLLA blocks in the copolymers. With the addition of longer PLLA blocks onto the PEG center, the copolymers may have even lower melting temperature that are lower than the body temperature. Using a much higher molecular weight PEG as a center block might be able to resolve this issue even with a much longer PLLA chain. Incorporating other polyester hard block onto the PEG center block with a higher melting temperature could be worth trying such as polyglycolide (PGA). The mixture of polyesters including polycaprolactone (PCL), PGA and PLLA onto the PEG center block is another approach.
This will keep the ending groups of the copolymer biodegradable but changing the melting temperature of the copolymers.

6.3 Elasticity

The synthesized copolymers are proved to be thermoplastics but it’s a quite rigid material once it is cooled to room temperature. Cohn and Hotovely-Salomon introduced the chain extension of PLA-PEG-PLA using hexamethylene diisocyanate (HDI) which performs as a crosslinker that creates highly flexible thermoplastic elastomers based on PLA-PEG-PLA triblock copolymers and the morphology of both the copolymer and the extended copolymers are the same [3]. The resulting material has an elongation at break level above 1000% and the ultimate tensile strength reaches 30 MPa. The introduction of crosslinker for the copolymers may be able to modify the mechanical properties that allows the material to be more elastic and flexible.
7.0 REFERENCES


8.0 APPENDICE
Appendix A: Thesis Signature Page